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B3H 3Z1

THE USE OF MICROBES IN THE DE-WATERING OF FUEL GRADE PEAT

Part 2

D.G. Cooper
D.S. Glass
D.W. Pillon

Department of Chemical Engineering
McGill University
3480 University Street
Montreal, Canada

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Principal Investigator:	Dr. D.G. Cooper	- McGill
Scientific Authority:	Mr. T.E. Tibbetts	- NRC
Project Scientist:	Mr. J.D. Sheppard	- NRC
Science Procurement Manager:	Mrs. J.P.S. Sztramko	- SSC

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Executive Summary

Part 1 of this research had already demonstrated the feasibility of using microbial products such as polymers, surfactants and enzymes, to enhance the mechanical de-watering of fuel-grade peat. The most effective of the biological compounds was the polysaccharide chitosan. In its charged form it can increase the amount of water removed after pressing by up to 60%. A major aspect of the second year of this research was to study the application of this polysaccharide to peat drying in more detail.

Concentration studies have shown that the optimum concentration of chitosan is .030 g/g of peat solids in the slurry. It is possible to further improve the extent of water loss by adding a heat pretreatment step before the addition of chitosan. The heat pretreatment used was relatively mild. The maximum temperature used was 200° C. By varying the length of the heat pretreatment and the maximum temperature, it was shown that as the amount of thermal energy increased, the quantity of extra water released after pressing also increased. However, after about 175° C the increase in the amount of water removed started to decrease and it would not probably be worth the extra cost to use higher temperatures in a commercial process.

The effects of chitosan and heat were additive at all the preheating conditions studied. However, the magnitude of the improvement as a result of the chitosan was largest at lower temperatures. In the experiments with the highest temperatures and energy input, there is still a marked improvement if chitosan is

added but probably not enough to make the addition economic.

The economic significance of the chitosan addition is seen at low pretreatment temperatures. By adding chitosan, the effect of the de-watering is the same as a much higher pretreatment temperature. This dramatically reduces the amount of energy that is needed for de-watering and improves the overall energy balance for the process.

The chitosan has a second effect on the economics of the process. No matter what temperature or procedure is used, there is a potential pollution problem in the dissolved and suspended solids in the large quantities of released water. In every experiment that chitosan was added, there was a significant improvement in the quality of the expressed water. The particles of suspended solid were larger than the control experiments and settled out much more quickly. This gave a clear aqueous phase and a relatively compact sludge which would be recycled into the press in a commercial process. This would have two effects: it would reduce water treatment costs and increase the amount of solids recovered from the original peat slurry.

The above results can be explained by two mechanisms- aggregation of colloidal particles by the chitosan polyelectrolyte and chemical alteration by thermal pretreatment.

The chitosan has all the properties of a polyelectrolyte. Our results show that it increases the average particle size of the peat solids after pressing. The mechanism is probably a combination of; coagulation by suppression of the negative charges on

the colloidal particles due to the quaternized amines on the chitosan, and; flocculation by bridging between particles by the charged polymers. Synthetic polyelectrolytes have the same effect. Inorganic salts, such as $FeCl_2$ and $AlCl_3$ caused some improvement but are not as efficient. This is probably because they lack the bridging potential.

The heat pretreatment would result in the loss of carboxylate and other polar functional groups on the peat solids. This would decrease the binding of water molecules due to dipole-dipole and ion-dipole interactions. Some of the water molecules could be released by either agency and at high pretreatment temperatures much of the water the chitosan could have released, would have been freed by the loss of polar groups.

The final objective of this part of the research was to further elucidate the growth characteristics of microbes on the expressed water. It had already been shown in part 1 that many microorganisms could be grown on the expressed water. This reduces the amount of dissolved solids in the water and produces valuable microbial products. Using one organism, Xanthamonas campestris, as a model system, we have been able to do continuous fermentations with peat water as the feed stock. In a commercial process the water stream would be put continuously through fermentors. The product would be recovered. The solids would be returned to the press and the water would be returned to the environment.

Résumé administratif

Dans la première partie de la présente recherche, on a démontré qu'il était possible d'utiliser des produits microbiens tels des polymères, des agents de surface et des enzymes pour améliorer la déshydratation mécanique de la tourbe combustible. Le plus efficace des composés biologiques était le chitosane. Lorsqu'il est chargé, ce polysaccharide permet d'accroître de jusqu'à 60 % la récupération d'eau après pressage. La deuxième année de recherche a été principalement consacrée à l'étude détaillée de l'utilisation de ce polysaccharide dans le séchage de la tourbe.

Des études de concentration ont montré que la concentration optimale de chitosane était de 0,030 g/g de solides tourbeux dans la bouillie. Il est possible d'accroître encore plus la perte d'eau en faisant précéder d'un prétraitement thermique l'addition du chitosane. Le prétraitement thermique utilisé était relativement doux. La température maximale a été de 200°C. En faisant varier la durée du prétraitement thermique et la température maximale, on a observé que la quantité d'eau supplémentaire produite après pressage augmentait avec la quantité d'énergie thermique. Cependant, passé environ 175°C, la quantité d'eau supplémentaire produite commençait à diminuer et il ne serait probablement pas rentable de dépenser plus pour atteindre des températures plus élevées dans un traitement commercial.

Les effets du chitosane et de la chaleur s'ajoutaient dans toutes les conditions de préchauffage étudiées. Cependant,

l'amélioration consécutive à l'addition de chitosane était la plus grande aux basses températures. Dans les expériences à températures élevées et avec de grands apports de chaleur, on a observé encore une nette amélioration par ajout de chitosane, mais cette amélioration n'est probablement pas suffisante pour que l'addition du produit soit rentable.

L'addition de chitosane se révèle économiquement rentable à basse température de prétraitement. Elle a le même effet sur la déshydratation qu'un prétraitement à température beaucoup plus élevée. On réduit donc ainsi considérablement la quantité d'énergie nécessaire pour la déshydratation et on améliore le bilan énergétique global du traitement.

L'addition de chitosane a un deuxième attrait économique. Quelle que soit la température ou la méthode utilisée, la présence de solides dissous ou en suspension dans les grandes quantités d'eau produites crée un risque de pollution. Dans toutes les expériences à ajout de chitosane, on a noté une nette amélioration de la qualité de l'eau exprimée. Les particules de solides en suspension étaient plus grosses que dans les expériences témoins et elles se déposaient beaucoup plus rapidement. On obtenait ainsi une phase aqueuse transparente et une bouillie relativement compacte qui pourrait être recyclée dans la presse dans un traitement commercial. L'addition de chitosane aurait deux effets : elle permettrait de réduire les coûts de traitement de l'eau et d'augmenter la quantité de solides récupérés de la bouillie de tourbe originale.

Les résultats ci-dessus peuvent s'expliquer par deux mécanismes, à savoir l'agrégation de particules colloïdales due à la

fonction polyélectrolyte du chitosane et l'altération chimique due au prétraitement thermique.

Le chitosane présente toutes les propriétés d'un polyélectrolyte. Nos résultats montrent qu'il augmente la taille moyenne des particules de solides tourbeux après pressage. Le mécanisme est probablement une combinaison de deux effets, à savoir la coagulation consécutive à la suppression des charges négatives sur les particules colloïdales, attribuable aux amines quaternisées présentes sur le chitosane, et la flocculation consécutive à l'établissement de ponts entre les particules par les polymères chargés. Les polyélectrolytes synthétiques ont le même effet. Les sels inorganiques, tels $FeCl_2$ et $AlCl_3$, ont permis une certaine amélioration, mais ne sont pas aussi efficaces. Cela est probablement dû au fait qu'ils ne permettent pas l'établissement de ponts.

Le prétraitement thermique résulterait en la perte de groupes carboxyles et d'autres groupes fonctionnels polaires sur les solides tourbeux. Cela se traduirait par une diminution des ponts entre les molécules d'eau dus aux interactions dipôle-dipôle et ion-dipôle. Certaines molécules d'eau seraient libérées par l'un ou l'autre effet et, à des températures de prétraitement élevées, une grande partie de l'eau que le chitosane aurait permis d'extraire aurait été libérée par la perte de groupes polaires.

L'objectif final de cette partie de la recherche était de déterminer les caractéristiques de croissance de microbes sur l'eau exprimée. On a déjà montré dans la première partie qu'il est possible de faire croître de nombreux microorganismes sur l'eau

exprimée. Cela permet de réduire la quantité de solides dissous dans l'eau et de produire des substances microbiennes utiles. En utilisant le Xanthamonas campestris comme système modèle, nous avons pu réaliser des fermentations continues avec de l'eau de tourbe comme matière première. Dans un traitement commercial, l'eau circulerait de façon continue dans les réacteurs de fermentation. Le produit serait récupéré. Les solides seraient renvoyés dans la presse et l'eau serait déchargée dans l'environnement.

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Chapter 1

Introduction

1.1. INTRODUCTION

This research examines two pretreatment processes which aid in the mechanical de-watering of fuel grade peat: thermal pretreatment and biochemical pretreatment. The two processes are studied separately and coincidentally in an attempt to isolate and optimize their effects. Both colloid science and organic chemistry are used to describe how the pretreatment processes are believed to work. The thermal pretreatment process is discussed first and background on the bio-chemical process follows.

1.2. THE THERMAL PRETREATMENT PROCESS

As early as 1850 it was known that the water-bonding structure of peat could be broken down by heating it[1]. Since the mid-nineteenth century raw peat has been thermally treated in a variety of different ways. These include both batch and continuous processes, with and without oxygen and under varying degrees of heat and pressure. Perhaps the simplest heating process is "wet carbonization". It is the wet carbonization process which most closely describes the heat treatment method used in this research.

In the wet carbonization process raw peat (solids content less than 15%) is heated at relatively low temperatures (180°-350° C) in a pressurized reactor. Residence times are usually less than one hour. Wet carbonization provides two benefits. It (1) promotes de-watering and (2) enhances the heating

value of the peat by improving the oxygen to carbon ratio. Our process uses a lower range of temperatures (50-200° C).

Although the benefits of heat treatment have been known for over a century accepted mechanisms of how the peat is altered, chemically and/or structurally, have yet to be developed. This research is difficult because peat is a very heterogeneous matter. This heterogeneity is due to the wide range of plant matter that collects in a single bog and the large number of routes of decomposition which yield the formation of peat.

Chemically, peats are composed mostly of organic material. The small percentage of inorganic materials (2-10%) usually present does not have a significant effect on de-watering characteristics. The organic materials exist as an enormously complex mixture derived from chemically stable residues of plant tissues.

A number of methods have been used to chemically classify peat substances. One system uses several broad categories to group the organic components in peat. Each category is characterized by its solubility in a standard solvent. Those substances which can be dissolved by suitable organic solvents are bitumens. Bitumens encompass waxes and "resinous" materials. A second category, humic acids, are soluble in aqueous base and precipitated by acidification of the alkaline extract. A third group which is characterized by its solubility in acid includes carbohydrates related to cellulose and some protein like substances. The fourth group consists of the lignins which are soluble in strong base and are characteristically phenolic in their reactions[2].

In the low temperature process studied here only three of the above classes of compounds are of interest: the humic acid fraction, the carbohydrates and the lignins. It is these three classes of peat constituents which are most likely to undergo chemical changes during heating. The bitumens are among the last distinguishable components to break down or volatilize when peat is exposed to heat[2]. Generally, they begin to undergo chemical changes at 350° C, however, physical changes may occur at lower temperatures.

Because there exists no accepted conventions on procedures for separating peat compounds, and, furthermore, because each peat sample is different in its chemical makeup, the distinction between classes and even the characterization of the classes is often very subjective. Many authors tend to define the categories in their own way. However, an attempt to describe the humic acids, lignins and carbohydrates commonly found in peat follows.

Humic acids, which are extracted from peat by dilute alkaline media, are amorphous, brown or black, hydrophilic, acidic, polydisperse substances of molecular weights ranging from several hundreds to tens of thousands[3]. This fraction can represent up to 40% of the dry weight of peat. After alkaline extraction of peat, acidification of the solution causes precipitation of the humic acids, however, another class of compounds, fulvic acids, remain in solution. Fulvic acids are closely related to humic acids. They differ principally in molecular weight and functional group content, with the fulvic acid fraction having a

lower molecular weight but higher content of oxygen containing functional groups per unit weight. A wide variety of chemical degradation experiments on humic acids and fulvic acids have shown that the major degradation products are phenolic and benzenecarboxylic acids. Schnitzer has suggested that these benzene carboxcylic acids and phenolic acids are the "building blocks" of humic and fulvic acid. He believes that the molecular forces holding the "building blocks" together are similar in both fractions, consisting mainly of hydrogen bonds, van der Waal's forces and π-bonding[4].

Lignins are closely related to humic acids chemically; both substances are polyphenolic in character[2]. The lignin fraction can be extracted from peat with a strong base. Between 10 and 15 percent of the dry weight of peat is lignin. The fundamental structural unit of lignin is a phenol substituted in the para-position by an n-propyl chain and in one or both ortho-positions by methoxyl groups. These units can be linked to each other in many ways, ususally through oxygens bonded to the carbons of the propyl group.

Because both the lignin fraction and the humic acid fraction can be extracted from peat with base, some authors do not distinguish between the two. The principal differences are (1) the predominant functional group in humic acids is the carboxyl group (about 8 mmoles/gram) which is not found in lignin's structure, (2) the solubility in dilute alkali of humic acid but not of lignin and (3) the high concentration of methoxyl groups in lign-

in; in humic acid methoxyl group concentration is about 0.2 mmol/g.

Carbohydrates are the third group of peat compounds to be considered. The most abundant carbohydrates found in peat can be further separated into four groups. They are hemicelluloses, chitin, glycosides and cellulose. Hemicelluloses are highly complex substances. Each molecule consists typically of 200-300 sugar monomer units. The hydrolysis of peat hemicelluloses yields glucose, fructose, mannose, galactose and xylose, among others[2]. Chitin, which is commonly found in the cell walls of microorganisms, is a linear polymer of N-acetyl glucoseamine. The third type of carbohydrate found in peat, glucosides, constitute a varied group of substances consisting of sugars bonded to noncarbohydrate molecules. Finally, cellulose, which is a polymer of glucose molecules, is the principal material found in the fibrous parts of plants.

In typical wet carbonization processes (temperatures above 200° C) it is known that the chemical structure of peat undergoes significant changes. It is these chemical changes which are believed to facilitate the de-watering of heat treated peat. Less work has been done on heat treatment processes below 200° C. However, as shown in chapter 7, even at 75° C peat de-watering is enhanced significantly. Only a small amount of research has been devoted to characterizing the chemical reactions peat undergoes when heated under these low severity conditions.

Chornet, et. al.[1] studied a low severity wet carbonization process in which peat was heated to 90° C and 190° C for

residence times of approximately one minute. Their main goal was to use shorter residence times to achieve breakdown of the hydrophilic nature of the peat substrate[1]. Specifically, they believe that short residence times are sufficient for hydrolytic reactions to occur. These reactions are reported to be acid catalyzed and cause the destruction of the hydrogen bonding which exists in the carbohydrate fractions, hemicellulose and cellulose. The principal chemical changes recorded in this process where: (1) a fifty percent reduction in the base soluble-acid soluble material (this corresponds to the fulvic acid fraction described earlier) and (2) an increase in carbon content and a decrease in oxygen content in the processed peat.

Fuchsman[2] describes the chemical processes peat undergoes during heating in considerable detail. The effect of wet carbonization (temperatures of 180°-220° C) on the de-watering properties of peat are again attributed to the breakdown of the highly hydrogen bonded molecular structure of peat[2]. The principal chemical changes during heating of peat at low temperatures are the decarboxylation of the carboxylic groups in the hemicelluloses and humic acids. The reactions up to 300° C, he explains, are easily idealized by low-temperature reaction mechanisms, e.g. loss of CO_2 by decarboxylation of acid groups, dehydration by splitting off water from hydroxylated aliphatic structures and generation of low-molecular-weight alcohols by simple rearrangements of esters.

Schnitzer and Khan[3] have done extensive work with humic acid and fulvic acid. Thermal degradation studies were done with

both substances. Analysis of DTG curves lead them to attribute low-temperature peaks to the elimination of functional groups. The most dramatic change in functional group concentration observed below 200° C was loss of approximately 10% of the carboxylic acid groups in fulvic acid. The main reactions governing the pyrolysis of humic acid are believed to be a) dehydrogenation (up to 200° C); b) a combination of decarboxylation and dehydration (between 200° and 250° C); c) continuous dehydration. The main reaction determining the pyrolysis of fulvic acid is dehydration.

REFERENCES

1. Chornet, E., Farell, K., Overend, R. and Roy, C. 1981. A low severity heat de-watering technology. In Proceedings of the IGT Symposium, Arlington, Va., Dec. 1, 1981. pp. 217-237.

2. Fuchsman, C.H. 1980. "Peat, Industrial Chemistry and Technology".

3. Schnitzer, M., Khan, S. 1972. "Humic Substances in the Environment". Marcel Dekker, Inc., N.Y.

4. Schnitzer, M., Khan, S. 1978. "Soil Organic Matter". Elsevier Scientific Publishing Company, N.Y.

Chapter 2

Coagulation

2.1 Introduction

Almost all natural surface waters contain particulate matter and/or colloidal substances that are not removed rapidly by sedimentation. Consequently, it is necessary to catalyze their removal by physical and/or chemical coagulation.

Clarification of water was employed by early civilizations. Since these times, the predominate chemical agent has been alum (aluminum sulfate, $Al_2(SO_4)_3$). Other agents, such as, lime ($Ca(OH)_2$), ferric sulfate ($Fe_2(SO_4)_3$) and ferric chloride ($FeCl_3$), have also been used as well as biological material, such as, almonds, beans, nuts, toasted biscuits and Indian meal[1].

The chemical coagulation of turbid waters involves the interaction of particulate and/or colloids with a destabilizing agent. The essential purpose of coagulation is to aggregate these particles into larger sizes that will settle quickly. In the case of peat, these larger aggregations should allow more of the water present to be removed by mechanical pressing. This aggregation process is called destabilization of colloidal systems.

In coagulation processes, the electrical double layer surrounding the colloid particles is discharged by addition of suitable reagents. The effectiveness can be measured by investigation of the zeta potential of the colloidal particles in these systems[2]. This discharge is due to the addition of ions of opposite electrical sign to the colloidal-containing system. Since most colloidal particles are negatively charged in aqueous systems[3], such as, peat, the useful ions for discharge are cations.

In pure coagulation reactions, the double layer is repressed by the cationic "counterions". This leads to a drastic reduction in the repulsive forces between colloidal particles. These particles can then approach and collide with one another more effectively, so that the very short range, attractive Van der Waal's forces, which are always present between particles, can come into play, resulting in agglomeration[4].

The resulting coagulum constitutes a dense phase since the individual colloid particles tend to pack together due to the drastic reduction in charge repulsion. The coagulum tends to be relatively impermeable to water drainage and, therefore, can give rise to water retention.

Another process is flocculation. In flocculation, the basic mechanism is the bridging of colloid particles by long-chain polymer molecules[5]. Discharge of double layers is often completely absent, as when negative charged colloids are flocculated by negatively charged polymers. Flocculation is usually more effective with increasing molecular weight of the polymer allowing for a greater geometric extension in the system and a greater number of attachments it can form. Flocculation results typically in the formation of loosely packed flocs which enhances their permeability to water. Since the electrical double layer has often not been discharged in flocculation, electrostatic repulsion may still be operative, preventing the type of close packing of the reacted colloids which is characteristic of coagulation. The loose packing often results in better water drainage.

Sedimentation can be used to remove suspended particles down to a size of about 50 μm depending on their density. However, particles smaller than 50 μm have very low settling velocities so that removal by sedimentation is not feasible. Table 2.1. gives calculated settling velocities for particles with specific gravities of 2.65 in water at 10°C[6]. Therefore, colloidal particles which are smaller than 50 μm must be agglomerated in order to be removed from water systems.

2.2. Chemistry of Coagulants

Aluminum and iron cations undergo hydration reactions in aqueous systems to an extent governed by the ligand properties of the cation, the metal ion concentration and the $[H^+]$ concentration[7]. That is, "naked" metal ions do not exist in water, but occur as aquocomplexes of varying degrees. The addition of Al (III) and Fe(III) salts to water at concentrations lower than the solubility product constants of their amorphous hydroxides leads to the formation of soluble monomeric, dimeric and polymeric hydroxometal complexes. It should be noted that both Al and Fe are amphoteric, that is, both cationic and anionic complexes are formed.

Whenever the solubility product constants are exceeded for $Al(OH)_3$ and for $Fe(OH)_3$, a series of hydrolytic reactions occurs[8]. Amorphous forms of the metal hydroxides eventually precipitate. The significance of this is that the polymeric forms (i.e.

Table 2.1. Settling Velocities for Spherical Particles[a,8]

Particle Size (μm)	Settling Velocities (m/h)	Time Required to Settle
1000	6×10^{2}	3s
100	2×10^{1}	38s
10	3×10^{-1}	33m
1	3×10^{-3}	55h
0.1	1×10^{-5}	230 days
0.01	1×10^{-7}	6.3 yr

a. Particles with a specific gravity of 2.65 in water at 10°C

b. Calculations based on sphere with a specific gravity of 2.65 to settle 1 ft.

hydrometal complexes) are adsorbed onto the colloidal particles and cause their destabilization. The quantity of coagulant required for coagulation depends on the quantity of colloids in the water and this relationship describes the stoichiometry of the coagulation reaction[9].

In general, there are two mechanisms of coagulation. One is neutralization of surface charges on the colloid by positively charged cations of Al and Fe or their hydrous oxides. In this case, it is not necessary to achieve electroneutrality. Rather, a reduction in the zeta potential frequently results in destabilization of the colloids. The second mechanism is physical entanglement of the colloid with floc. In this case, the zeta potential of the colloid is low or, at least, very close to the point of destabilization.

Polyelectrolytes, long-chain organic molecules, are also employed as flocculants. They can be either cationic, anionic or nonionic materials and they can be further characterized by their molecular weight, structure and extent of electrical charge.

Anionic polyelectrolytes are negatively charged with the most common type of anionically charged group being the carboxylate moiety ($-COO^-$). These carboxylate groups are distributed along the polyelectrolyte chain with acrylamide being the most common recurring unit. The carboxylate groups are interspersed throughout the polymer by hydrolysis of some of the amide groups. Moieties such as carboxylic acids are relatively weakly ionized, therefore, only a fraction of these are in the

carboxylate form ($-COO^-$). This class of anionic polyelectrolytes are refered to as "weak" polyelectrolytes.

Other types of anionic polyelectrolytes are much more highly ionized, a common example being polystyrene sulfonic acid. These materials are extensively ionized down to very low pH levels and they are referred to as strong polyelectrolytes. They possess a high level of charge, which is little influenced by the pH of the solution. Intermediate types also occur, such as polyelectrolytes possessing phosphonic acid groups with acid strengths between the weak and strong anions.

The term "nonionic" polyelectrolyte is rather misleading since electrolytes are by definition ionic. However, it generally means that the charge level of the polyelectrolyte is very low and the charge has not been deliberately placed in the polymer by hydrolysis or copolymerization.

The most common examples of nonionic polyelectrolytes are polyacrylamides containing a small fraction (0.5 to 1%) of carboxylate ions. This low charge level precludes any significant extension of the polymer chain due to mutual charge repulsion along the chain.

Cationic polyelectrolytes have positive charges on the polymer chain with the most common groups being amino ($-NH_3^+$), imino ($-NH_2^+-$) and quaternary amino ($-NR_3^+$). The first two are weak bases in the same sense as the carboxyl group is a weak acid, while the quaternary amino group is a strong base (analogous to the strong acid sulfonate group). The charge levels of the amino

and imino containing polyelectrolytes are strongly dependent on pH, while the charge level of the quaternary ammonium group is relatively independent of pH. Again, various proportions of these functional, chargeable groups may be contained on different grades of polyelectrolytes. Cationic polyelectrolytes usually function by a combination of charge-neutralization and bridging mechanisms.

References

1. Baker, M.N. 1981. "The Quest for Pure Water". American Water Works Association. Denver.

2. Ruddick, J.M. 1968. "Control of Colloid Stability Through Zeta Potential". Zeta-Meter Inc. New York.

3. Christman, C.H. J. Am. Water Works Assoc. 21:1076(1929).

4. O'Melia, C.R. 1972. "Physiochemical Processes for Water quality Control". W.J. Weber, Ed. John Wiley and Sons. New York.

5. La Mer, U.K. 1967. "Principles and Applications of Water Chemistry". Faust, S.D. and Hunter, J.V. Eds. John Wiley and Sons. New York.

6. Tebbutt, J.H.Y. 1983. "Principles of Water Quality Control". Pergamon Press. Oxford.

7. Faust, S.D. and Aly, O.M. 1983. "Chemistry of Water Treatment". Butterworths. Boston.

8. Sillen, L.G. and Martell, A.E. "Stability Constants of Metal-ion Complexes". Special Publications 17 and 25. Chemical Society. London (1964,1971).

9. Stumm, W. and O'Melia, C.R. J. Am. Water Works Assoc. 60:514 (1968).

Chapter 3

Project Background

3.1. Summary of Previous Results

Research done for the D.S.S. contract (no. ISU83-00030) demonstrated that several types of biological compounds, including polymers, surfactants and enzymes, can significantly enhance the mechanical de-watering of fuel-grade peat (Tables 3.1. and 3.2.). The most promising compounds were polyelectrolyte polysaccharides, such as chitosan (Table 3.1.) and biosurfactants (Table 3.2.) which cause extreme lowering of the surface tension of water (27mN/m), such as surfactin from Bacillus subtilis. The most difficult peat to de-water encountered in our study was that obtained from Barrington, N.S. The addition of biological de-watering agents before pressing this peat increased the amount of water removed by up to 60%.

A preliminary study revealed that combining heating pretreatment and biological additions caused substantially better de-watering than either process alone (Table 3.3.). If the Barrington peat was heated at 125°C for 20 min. before pressing, the amount of water removed was increased by about 60%. If the biological agents were added to the peat between heating and pressing the water released was increased by 100%.

The water expressed from the various peat samples with the use of various additives and treatment procedures contained dissolved and suspended carbonaceous solids. With the addition of small amounts of other nutrients to these water samples, it was possible to grow many different bacteria and yeasts (Table 3.4.). Using the organic materials, expressed from the peat, as the

carbon source for these microorganisms it was possible to produce significant yields of biopolymers and biosurfactants. In particular, it was possible to produce the de-watering agents xanthan gum and surfactin.

This research has shown that the process outlined in Figure 3.1. is feasible. Biological materials can significantly improve the amount of water removed from peat by pressing. The BOD of the expressed water can be reduced by using it as a substrate to produce the biological agents for de-watering as well as valuable excess materials.

There is good potential for using biological agents to improve other pretreatment processes. Thermal pretreatment methods have been proposed by J.P. Energy, I.G.T., Zimpro, Ontario Research Foundation and the University of Sherbrooke and they all have appreciable waste treatment requirements. The addition of biological agents to the peat in these processes would be expected to minimize the waste treatment by reducing the severity of the various methods of pretreatment. There is also excellent potential for utilizing the soluble carbon compounds in the expressed water as growth substrates to produce biopolymers, etc. Thus, our research has wide applicability. It is not limited to a single process and could be used to augment other methods of peat treatment.

3.2. Project Objectives

With the initial promising results it is necessary to show that an economic process is feasible. The best results were obtained with a mixture of pre-heating and addition of biological materials before pressing. It is essential to optimize this process on a laboratory scale before moving to larger scale. Heating increases water release, but it also increases cost and dissolved organics expressed with the water.

Another aspect of this research is the use of aerobic fermentations to treat the expressed water before returning it to the environment. This will reduce the pollution and yield valuable products such as polymers and surfactants.

A set of experiments was undertaken to study the effect of the various parameters on pretreatment. Work was continued on the room temperature process as well as heat pretreatment at temperatures of ~25° intervals up to 200°C. The parameters studied included:

1) length of preheating time
2) quantity and type of agent
3) effect of stirring

The amount of water removed and the quality of this water were monitored. The quantity of water expressed and the amount of suspended solids in the water demonstrate the efficiency of the process to produce the required dry peat solids. The quality of the water includes several measurements including colour, COD, suspended solids and toxicity.

The goal is an optimization of a relatively mild pre-treatment process which results in good water release and relatively little pollution. This data will allow a determination of the most efficient process by considering heating, quality of the expressed water, fermentation, amount of carbon recovered in the pressed solid and value of extra biological products. Implicit in these conclusions are a partial elucidation of the mechanism of de-watering of the peat.

Table 3.1. The Effect of Pretreatment with Chitosan on Water Removal from Peat after Pressing[a]

Peat Source	Ratio of Chitosan to Peat (wt/wt)	Amount of Water Removed (kg H_2O/kg dry peat)	Water Removed (%)	Moisture Content of Pressed Peat (%)
Quebec	control	3.84	60.1	71.8
Quebec	0.0016	4.39	68.7	66.7
Quebec	0.0024	4.71	73.7	62.7
Barrington	control	2.31	37.9	79.1
Barrington	0.0016	3.70	60.7	70.5
Ont. Res. Found.	control	3.36	63.4	66.0
Ont. Res. Found.	0.0016	3.83	72.3	59.5

a. Pressing Conditions, 2.5 min. at 19.3 atm.; 25g sample

Table 3.2. The Effects of Biological Additives on Water Removal from Peat by Pressing[a]

Peat Source	Additive	Amount of Water Removed (kg H_2O/kg dry peat)	Water Removed (%)	Moisture Content of Pressed Peat (%)
Quebec	control	5.04	65.1	73.0
Quebec	surfactin	6.02	77.8	63.2
Quebec	esterase[b]	5.99	77.4	63.6
Barrington	control	3.77	45.1	77.8
Barrington	surfactin	4.12	60.0	73.3
Barrington	esterase[b]	4.13	60.1	73.3

a. Pressing Conditions, 2.5 min. at 19.3 atm.; 25g sample

b. Sample incubated for 17h at 23°C with 0.05g esterase

Table 3.3. Pretreatment by Heating and Addition of Biological De-Watering Agents[a]

Thermal Pretreatment	Additive	Amount of Water Removed (kg H_2O/kg dry peat)	Water Removed (%)	Moisture Content of Pressed Peat (%)
control	control	2.31	37.9	79.1
120°C, 20 min.	control	4.16	62.5	69.6
120°C, 20 min.	chitosan	4.53	74.2	61.1
120°C, 20 min.	surfactin	3.22	63.0	65.5
control	chitosan	3.70	60.7	70.5

a. Pressing conditions, 2.5 min. at 19.3 atm.; 25g sample

Table 3.4. Examples of Growth of Microbes on Media Containing Peat Water as Carbon Source

Organism	Biomass (g/L)	Biopolymer Produce (g/L)	Surface Tension (mN/m)
Xanthamonas campestris[a]	1.0	1.7[d]	
X. campestris[a,b]	1.2	2.7[d]	
X. campestris[c]	0.5	0.4[d]	
Bacillus subtilis[a]	0.6		27
B. subtilis[a,b]	0.7		33
B. subtilis[c]	0.2		
Aureobasidium pullulans[a]	1.2	1.8[e]	

a. 0.1% peptone and 0.1% yeast extract added

b. Water from thermally pretreated peat

c. Control, distilled water plus 0.1% peptone and 0.1% yeast extract

d. Xanthan gum (polysaccharide)

e. Pullulans (polysaccharide)

CHAPTER 4

MATERIALS AND METHODS

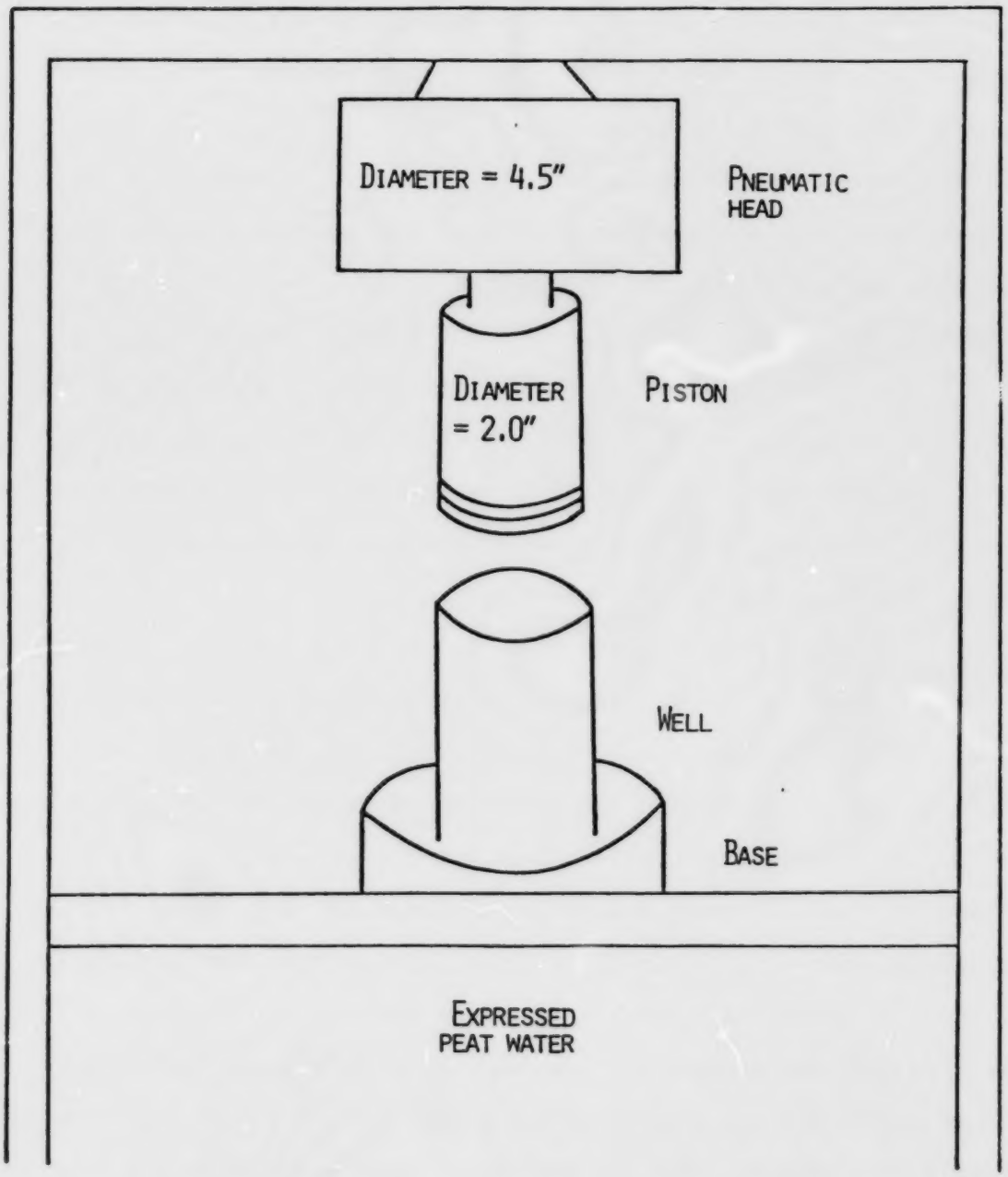
4.1. Mechanical Press

The blueprint for a peat pressing die was obtained from the Ontario Research Foundation. The die (Figure 4.1.) consists of a base with a shallow excavation in which a cylinder is rested. A sintered steel filter and a support disc are inserted into the cylinder and a piston, equipped with two o-rings for a tight fit, is used to apply pressure to the peat samples. The base has an aperture to allow the pressate to escape through the bottom.

In order to apply a maximum of 30 atm of pressure on the samples, a pneumatic system, with a pneumatic cylinder of 4.5 inches, connected to a 96 psi air line was employed. A double acting cylinder was chosen so that it could be used to insert as well as retract the piston of the press.

In order to integrate the die to the pneumatic system two modifications were necessary. First the piston was fastened to the pneumatic cylinder by boring the appropriate thread into the piston and screwing the two pieces together. The second modification consisted of fastening the cylinder of the press die to the base so that it would not be retracted with the piston. This was accomplished by driving three pins through the base and letting them protrude out slightly into the shallow encavement. Three inverted "L" shaped notches were then made in the peat cylinder to allow the two pieces to be quickly fastened or separated by a twisting motion. The equipment was then mounted on a stand capable of withstanding the forces at work. All modifications and assembly were performed by the Chemical Engineering Machine Shop.

Fig. 4.1. Mechanical Peat Press



4.2. STANDARD PRESSING PROCESURE

To a peat sample of approximately 25g was added the stated amount of biological agent. This mixture was stirred at 45 rpm for 5 minutes by means of a high torque stirrer. The sample was then transferred to the peat press where it was pressed for 3.0 minutes at 19.3 atm. After pressing, the sample was immediately weighed. The sample was then dried at 105°C to a constant weight.

4.3. CONTROL PRESSING PROCEDURE

The control procedure was the same as the standard pressing procedure except that no biological agents or heat was added.

4.4. CALCULATIONS OF THE WATER CONTENT OF PEAT

Water Content of the Unpressed Peat

$$\text{water content} = \frac{\text{wt of water in the sample}}{\text{wt of dry peat in the sample}} \quad (\text{kg } H_2O/\text{kg dry peat})$$

Water Content of Pressed Peat Samples

weight of water in pressed peat = wt of pressed sample - wt of pressed sample after drying

$$\% \text{ moisture content of pressed peat} = \frac{\text{wt of water in pressed sample}}{\text{wt of pressed sample}} \times 100$$

water content after pressing =

$$\frac{\text{wt of water in pressed sample}}{\text{wt of dry peat in pressed sample}} \quad (\text{kg } H_2O/\text{kg dry peat})$$

weight of water removed by pressing =
water content of unpressed peat - water content of pressed peat

$$\% \text{ water removed} = \frac{\text{wt of water removed by pressing}}{\text{wt of water in unpressed sample}} \times 100$$

4.5. PREPARATION OF THE CHLORIDE SALT OF CHITOSAN

The chitosan starting material was purchased from the Sigma Chemical Company, St. Louis, Mo. To 50mL of concentrated hydrochloric acid was added to 5 g of chitosan. The mixture was stirred and heated at 70°C for 2 hr. The solution was then cooled by means of an ice bath and acetone was added until a white precipitate appeared. The precipitate was collected by vacuum filtration and washed twice with 100 mL portions of acetone. The white solid was air dried.

4.6 PREPARATION OF XANTHAN DERIVATIVE

The xanthan gum starting material was purchased from the Sigma Chemical Company, St. Louis, Mo. To 100 mL of methanol, containing a catalytic amount of HCl, was added 10g of xanthan gum. The mixture was heated at reflux for 18h. To this solution was added 1g of the chloride salt of ethanolamine previously prepared by the addition of HCl (1mL) to 1g of ethanolamine. The mixture

containing the xanthan gum and the chloride salt of ethanolamine was heated at reflux for 24h. The resulting product (xanthan derivative) was washed with acetone and dried.

4.7. DETERMINATION OF CONCENTRATION OF SUSPENDED PEAT SOLIDS

Suspended peat solids were separated from a sample of expressed water and solutions of the five concentrations plotted in Figure 4.2 were prepared. The percentage absorbance of each sample was measured on the Hitachi Perkin-Elmer double beam spectrophotometer at 600 nm. Using linear interpolation and this curve provides an easy method for determining suspended solids concentrations in peat water samples.

4.8. STANDARD PROCEDURE FOR SETTLING RATE DETERMINATION

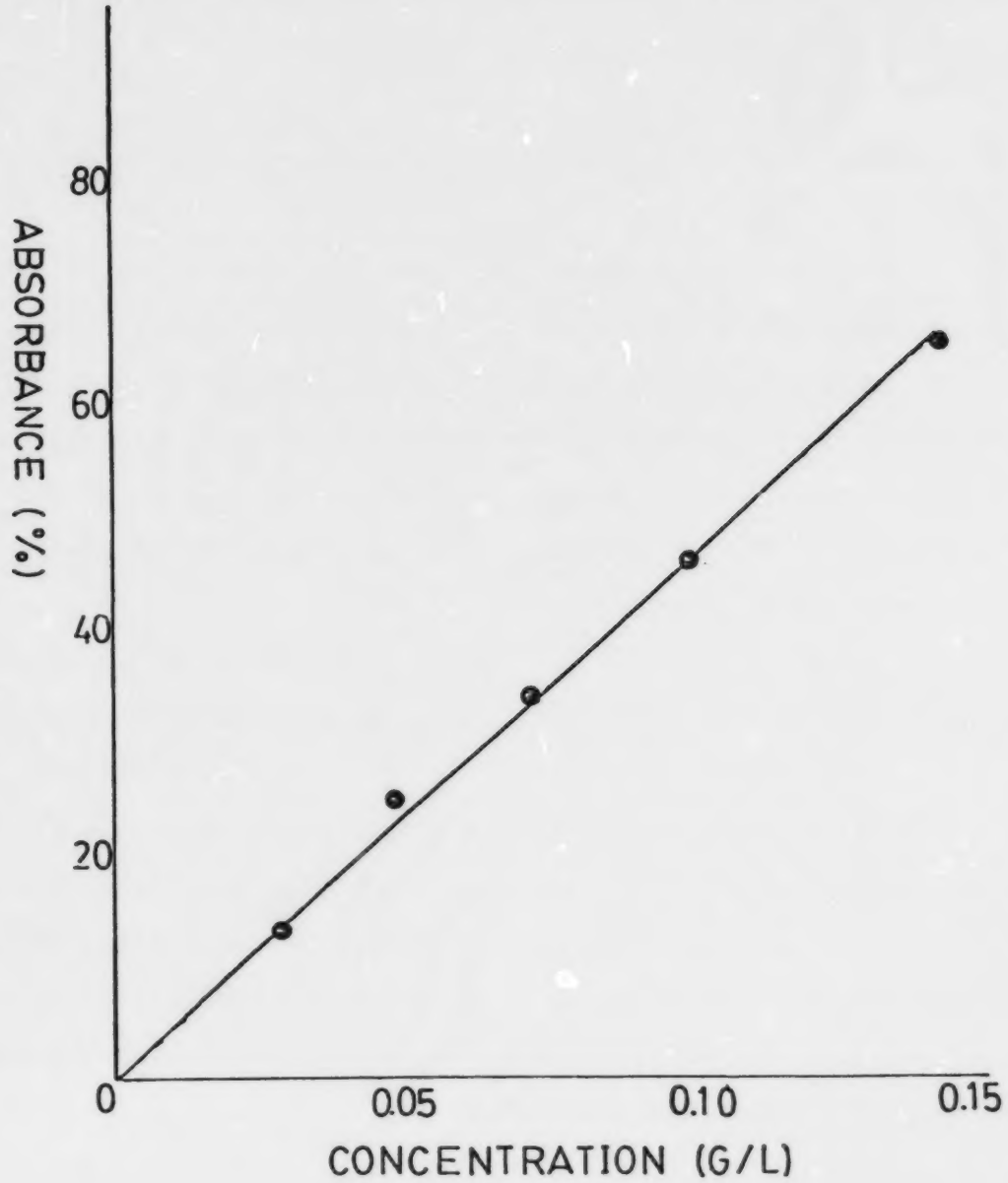
After a peat sample had been pressed, a 50 mg sample was taken and added to 10 ml of water. The solution was vortexed for 30s in order to resuspend the peat particles. The settling of the particles was followed by means of a spectrophotometer (600 nm). The initial reading was taken immediately after vortexing the sample. Another reading was taken after 1 h.

If: I = initial reading

F = final reading (after 1 h)

then: $$\% \text{ Settled, 60 min} = \frac{F-I}{I} \times 100$$

Fig. 4.2



4.9. MEASUREMENTS ON EXPRESSED WATER

Approximately 20 milliliters of expressed water is recovered from pressing after pretreatment. One milliliter is diluted with nine milliliters of distilled water. After vortexing for 30 seconds part of the solution is transferred to a cuvette and an immediate reading on the spectrophotometer allows calculation of the initial concentration of suspended solids. One hour later a second reading is taken. This allows calculation of percent settled after one hour, as described above.

4.10. STANDARD HEATING PROCEDURE

A Parr 4501 two-liter pressure reactor is used to heat peat to temperatures between 25° and 200°C. The jacket is first preheated and peat is added to the pressure vessel which is then sealed. After a determined amount of time the pressure vessel is placed into the jacket and allowed to reach the desired temperature. After the heat exposure cooling to room temperature is performed rapidly by immersing the vessel in cold water. The temperature is monitored by a Trutest dial thermometer placed in the thermowell which is immersed in the peat. After removal from the vessel the peat is pressed and its moisture content is determined.

4.11. HEATING WITH AN INERT ATMOSPHERE

Before being placed into the heating jacket the pressure vessel is flushed with nitrogen gas for fifteen minutes and then

sealed. The nitrogen is first bubbled through distilled water to prevent it from drying the peat. The standard heating procedure is then followed.

4.12. HEATING WITH STIRRING

During the standard heating procedure the peat is stirred at 100 rpm with the propeller stirrer attached to the head of the pressure vessel.

4.13. TOXICITY OF EXPRESSED WATER AND HEAT CONTENT OF HEAT TREATED PEAT.

Dried peat samples which had been exposed to a variety of pretreatment processes were sent to the NRC Atlantic Research Laboratory (Peat Program) for determination of calorific value. Expressed peat water samples were sent to the Ontario Research Foundation for "Microtox" tests.

4.14 BIOMASS DRY WEIGHT DETERMINATION

Ten grams of whole broth were centrifuged at 36,000 g for 20 minutes, washed in 10 ml of distilled water and then recentrifuged. The resulting pellet was washed into a preweighed aluminum dish and dried to a constant weight at 105°C.

4.15. XANTHAN DRY WEIGHT DETERMINATION

Five grams of cell-free supernatant obtained from the biomass analysis procedure were vortexed vigourously with 15 ml of methanol and centrifuged at 36,000 g for 15 minutes. The supernatant was discarded and the pellet was washed into a preweighed aluminum dish which was dried to a constant weight at 105° C.

4.16. VISCOSITY MEASUREMENT

For shake-flask experiments where the viscosity was relatively low a 40 ml sample was placed into a 50 ml glass beaker and analyzed using a Brookfield RVT viscometer (spindle 4 at 100 RPM). Due to the small size of the vessel and sample these measurements were not accurate. However they were reproducible and gave a good indication of the relative viscosity.

For the samples obtained from the fermentor a Brookfield LVT viscometer (spindle 3 at 30 RPM) was used. The small spindle size allowed for accurate viscosity measurement (i.e. no wall effects).

4.17. FERMENTATION CONDITIONS

A Multigen F-2000 2 liter fermentor (New Brunswick Scientific, Edison, New Jersey) was used. The temperature was maintained at 30° C, agitation at 540 RPM and the air flow rate always exceeded 1.0 VVM. This resulted in a maximum oxygen transfer rate

of 22.5 mM/l-h when the medium was free of xanthan. The pH was maintained at pH 7.0 by the automatic addition of 2.0 M NaOH. The fermentor was equipped with a water-cooled condenser.

FERMENTATION MEDIUM

The basic medium used is shown in Table 4.1.

4.18. GAS ANALYSIS

The exit gas flow rate from the fermentor was determined after passage through a drying column with a wet test meter. The oxygen concentration was determined paramagnetically (Taylor Sewomex Oxygen Analyzer OA 272) as by Fiechter and von Meyenburg[1].

4.19. REFERENCE

[1] Fiechter, A. and K. von Meyenburg, Biotechnol. Bioneg. 10:535 (1968).

Table 4.1 Growth Medium Composition

A) Mineral Salts Medium

Component	Concentration gL^{-1}
Glucose	Variable
$(NH_4)_2SO_4$	4
KH_2PO_4	2
$Na_2HPO_4 \cdot 7H_2O$	1
$MgSO_4 \cdot 7H_2O$	0.2
$CaCl_2$	0.02
Yeast Extract	0.1
$(CH_3COO)_2Zn \cdot 2H_2O$	0.016
$FeSO_4 \cdot 7H_2O$	0.003
H_3BO_3	0.006
$(NH_4)_6MO_7 \cdot 4H_2O$	0.006
HCl	0.3

pH adjusted with NaOH

B) YM Medium

Component	Concentration gL^{-1}
Glucose	10
Peptone	5
Malt Extract	3
Yeast Extract	3

CHAPTER 5

ENHANCED MECHANICAL DE-WATERING OF PEAT USING IONIC MOLECULES

In our previous report[1] it was shown that cationic polyelectrolytes, such as the chloride salt of chitosan, were effective in increasing water removal from peat by mechanical pressing. This study has been continued with the polyelectrolytes as well as being expanded to include inorganic salts which have proved useful in wastewater treatment processes[2]. In this investigation, Barrington, N.S., peat, which was supplied by the National Research Council's Atlantic Research Laboratory, was used for all mechanical pressing studies.

5.1. Polyelectrolytes

Three polyelectrolytes were tested. Two of these, Praestol 411K and Praestol 444K, are commercially available synthetic polymers while the third is the chloride salt of chitosan. From our previous report[1], all three of these polyelectrolytes proved useful in enhancing water removal by mechanical pressing. However, there was no attempt to optimize this procedure. Therefore, each polyelectrolyte was added to peat samples at various concentrations. At the same time, water removal was compared to particle settling by taking a sample of the pressed peat pellet and resuspending it in water and determining the settling rate of these particles after 1 h.

Initially, the chloride salt of chitosan was studied. The salt was prepared by treating chitosan with HCl. The results are shown in Table 5.1. When peat was mechanically pressed without chitosan only 32.1% of the water was removed. When chitosan

Table 5.1. The Effect of the Chloride Salt of Chitosan on Mechanical De-Watering of Barrington Peat and on Peat Particle Settling

Ratio of Chitosan to Dry Peat (wt/wt)	Number of Charged Sites ($X10^{20}$)	Amount of Water Removed (kg H_2O/kg dry peat)	Water Removed (%)	Moisture Content of Pressed Peat (%)
Control	-	2.34	32.1	83.2
0.004	0.28	3.25	44.7	80.1
0.019	1.15	4.68	64.3	72.1
0.030	2.32	4.65	63.9	72.4
0.042	2.89	4.49	61.7	73.6
0.050	3.46	4.43	60.9	74.0

Total Water Content = 7.28 kg H_2O/kg dry peat
% Water Content = 87.9%

was added, the water removal improved to 63.9% (0.07g of chitosan or 0.030 wt chitosan/wt dry peat in the sample). The water removal increased as the concentration of chitosan was increased. However, when concentrations over 0.07g (or a ratio of 0.030) were used, the water removal began to decrease (Table 5.1.). The particle settling rate of each pressed sample was also investigated (Table 5.1.). Again, the rate increased as the chitosan concentration increased. The maximum settling rate occurred at a chitosan concentration that was very close to the chitosan concentration (ratio of ~ 0.030) where the maximum rate of water removal occurred. This seems to indicate that coagulation plays a major role in the mechanism of the water removal process. This may be seen more clearly by examining Figures 5.1 and 5.2. The figures show that the water removal and particle settling rate follow the same pattern. The parameters increase at lower concentrations of chitosan and each reaches a maximum. After this maximum, each begin to decrease. Figure 5.3. compares these two variables, water removal and particle settling rate. Although the graph is almost linear, and demonstrates a correlation between these two parameters.

The investigation of the two synthetic polyelectrolytes was undertaken to determine whether this relationship between water removal and particle settling rate was unique to chitosan or whether it was a general result of the addition of polyelectrolytes. The results using the cationic, high charge, Praestol 444K, are shown in Table 5.2. As the concentration of Praestol 444K increased, the water removal increased, reaching a maximum of

Figure 5.1. Enhancement of water removal from peat with chitosan. Water removal (▲) and particle settling after 60 min (●) versus the ratio of chitosan to dry peat in the sample (wt/wt).

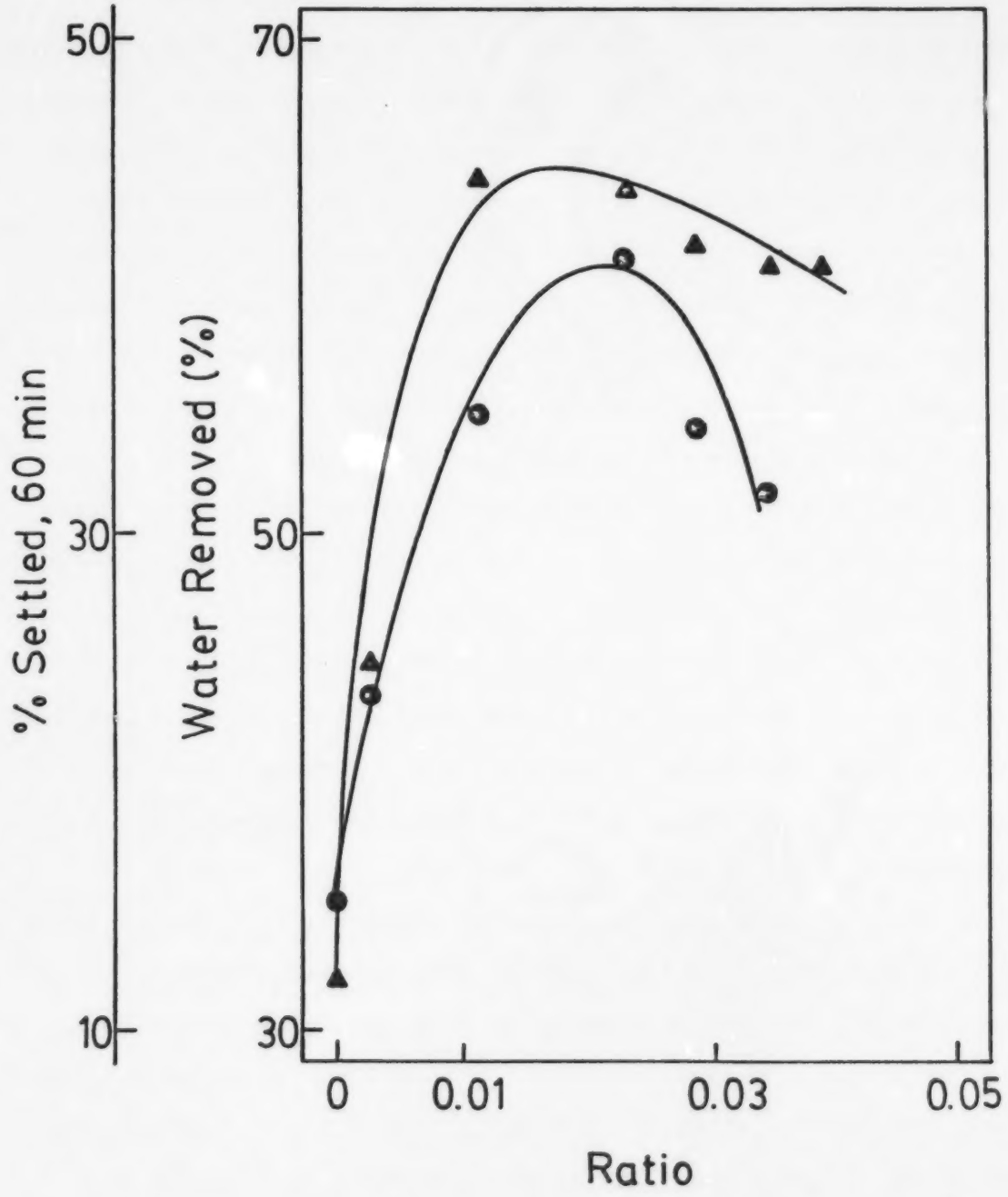


Figure 5.2 Enhancement of water removal from peat with chitosan. Water removal (▲) and particle settling after 60 min (●) versus the number of charged sites contained in the chitosan added to the peat sample.

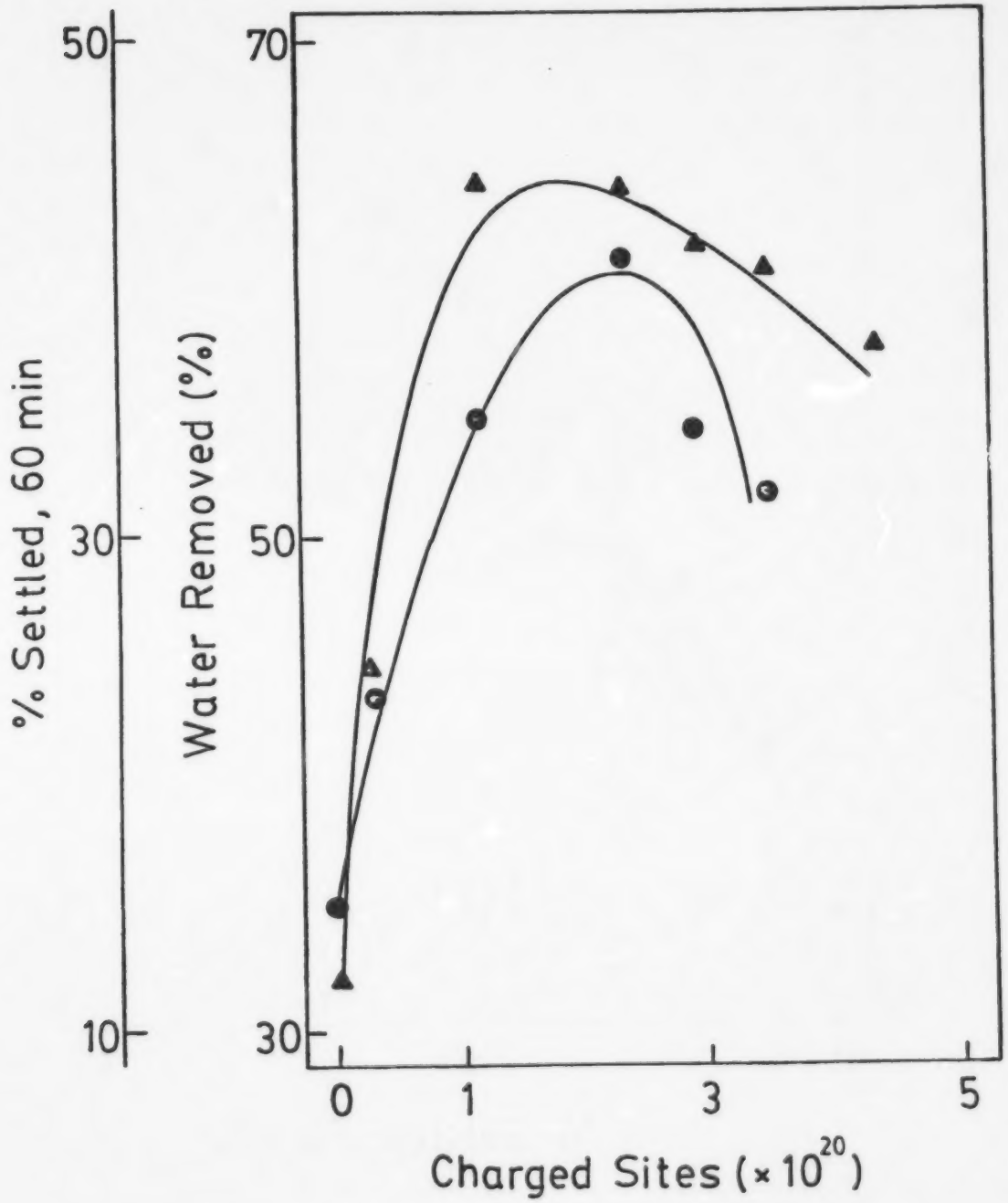
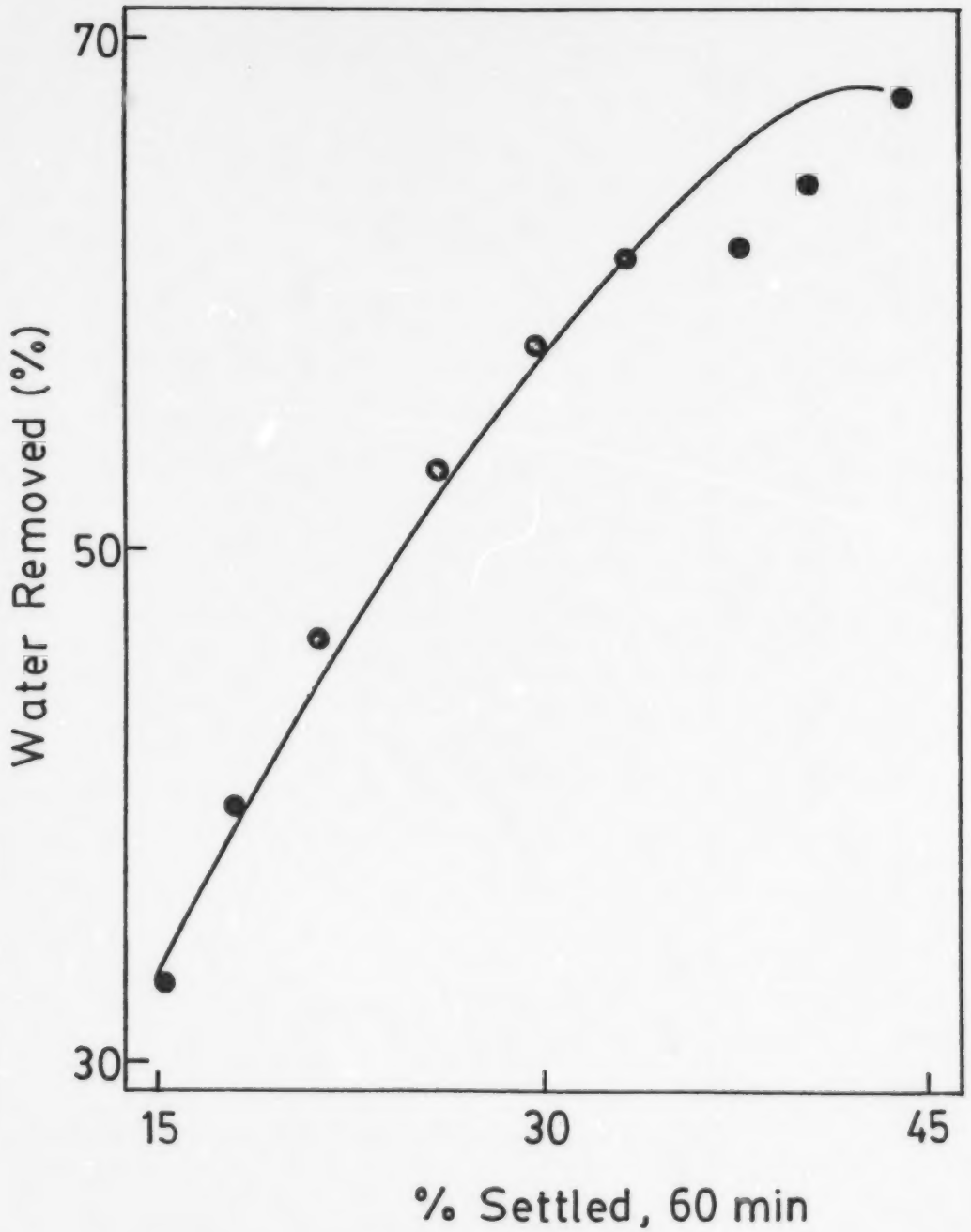


Figure 5.3. Enhancement of water removal from peat with chitosan. Water removal versus particle settling after 60 min.



62.4% (0.04g or a ratio of 0.015, Praestol 444K to dry peat in the sample). A similar result to chitosan was observed above this maximum as water removal began to decrease. However, for Preastol 444K, this decrease was much more dramatic since the highest concentration of the synthetic polymer removed only a little more water than the control sample no polyelectrolyte added. (Table 5.2.). Figures 5.4 and 5.5 clearly show that water removal is hindered at the higher concentrations of Praestol 444K. These samples were also observed to be very "sticky" or "gummy". This was not observed in the chitosan experiments. However, like the chitosan samples, the same pattern was present: an initial improvement in water removal followed by a decrease in water removal. Comparison of water removal and particle settling (Figure 5.6.) indicated a good correlation between these two parameters.

Finally, the cationic, low charge polyelectrolyte, Praestol 411K was tested. The results (Table 5.3.) were not as good as for the other two polyelectrolytes. The maximum water removal with mechanical pressing was 47.7%. The same pattern of a maximum in water removal followed by a decrease in water removal was observed (Figure 5.7.). Again there was a correlation between settling rate and water removal. Again, by examining Figure 6.8., it can be seen that a correlation exists between water removal with Praestol 411K and particle settling.

It is evident that all three of the polyelectrolytes studied enhance water removal by mechanical pressing. However, chitosan and Praestol 444K were far superior to Praestol 411K in water removal. These results indicate that coagulation and/or

Table 5.2. The Effect of the Cationic Polyelectrolyte, Praestol 444K, on Mechanical De-Watering of Barrington Peat and on Peat Particle Settling

Ratio of Praestol 444K to Dry Peat (wt/wt)	Number of Charged Sites ($X10^{20}$)	Amount of Water Removed (kg H_2O/kg dry peat)	Water Removed (%)	Moisture Content of Pressed Peat (%)
Control	-	2.34	32.1	83.2
0.004	0.290	3.97	54.5	76.8
0.015	1.16	4.54	62.4	73.3
0.031	2.03	4.02	55.2	76.5
0.039	2.90	3.21	44.1	80.3
0.057	3.77	2.62	36.0	77.6

Total Water Content = 7.28 kg H_2O/kg dry peat
% Water Content = 87.9%

Figure 5.4. Enhancement of water removal from peat with Praestol 444K. Water removal (▲) and particle settling after 60 min (●) versus the ratio of Praestol 444K to dry peat in the sample (wt/wt).

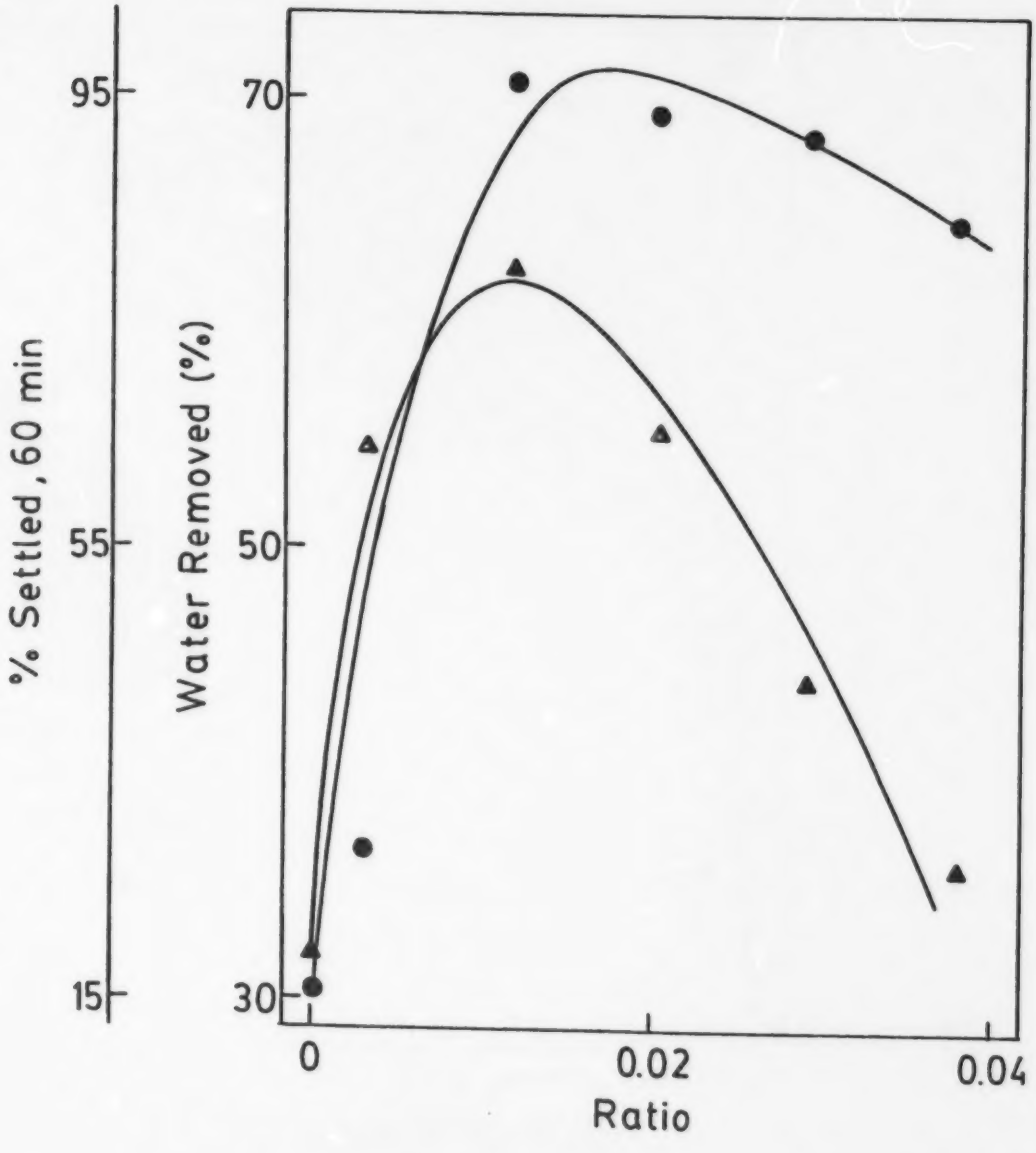


Figure 5.5. Enhancement of water removal from peat with Praestol 444K. Water removal (▲) and particle settling after 60 min (●) versus the number of charged sites contained in the Praestol 444K added to the peat sample.

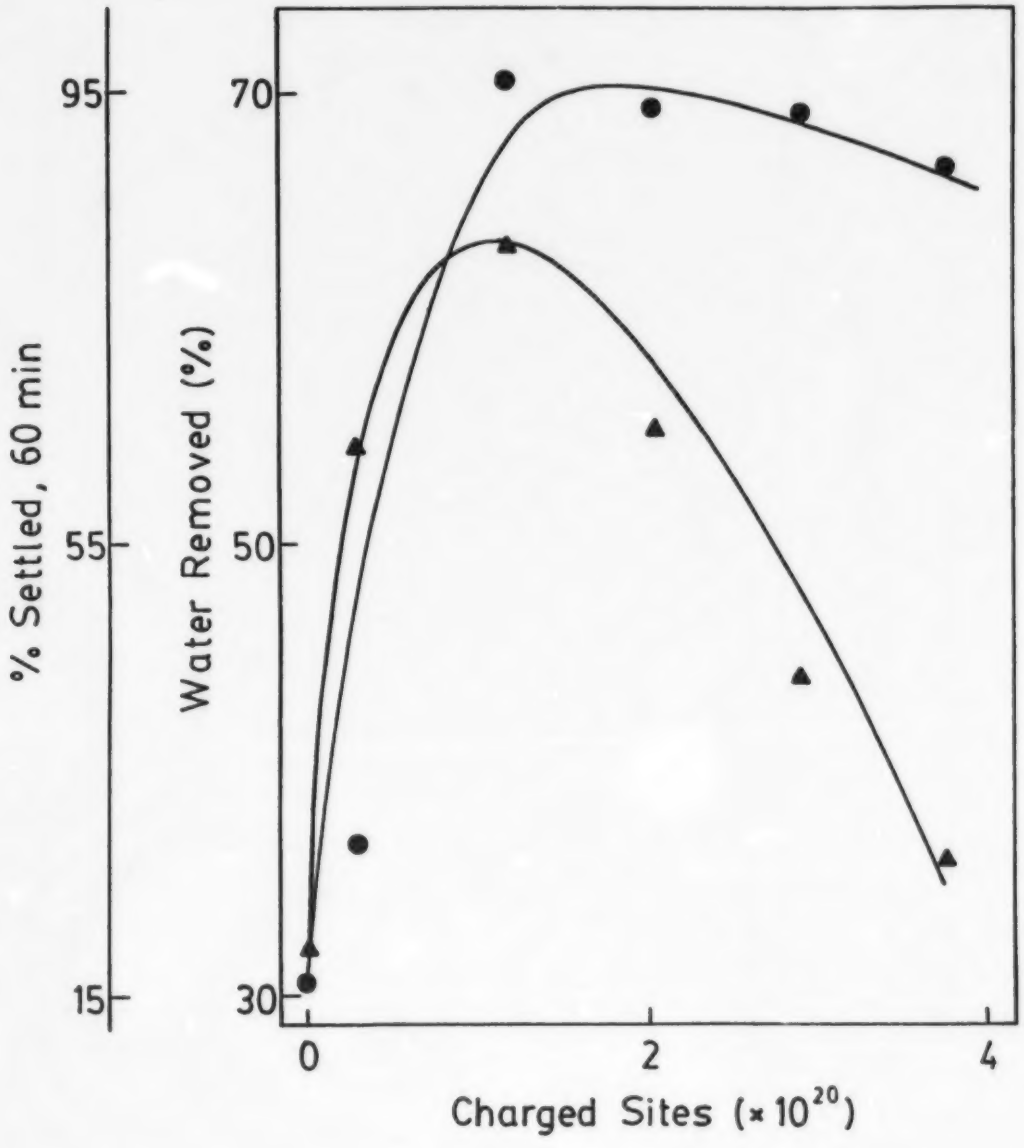


Figure 5.6. Enhancement of water removal from peat with Praestol 444K. Increased water removal versus particle settling after 60 min.

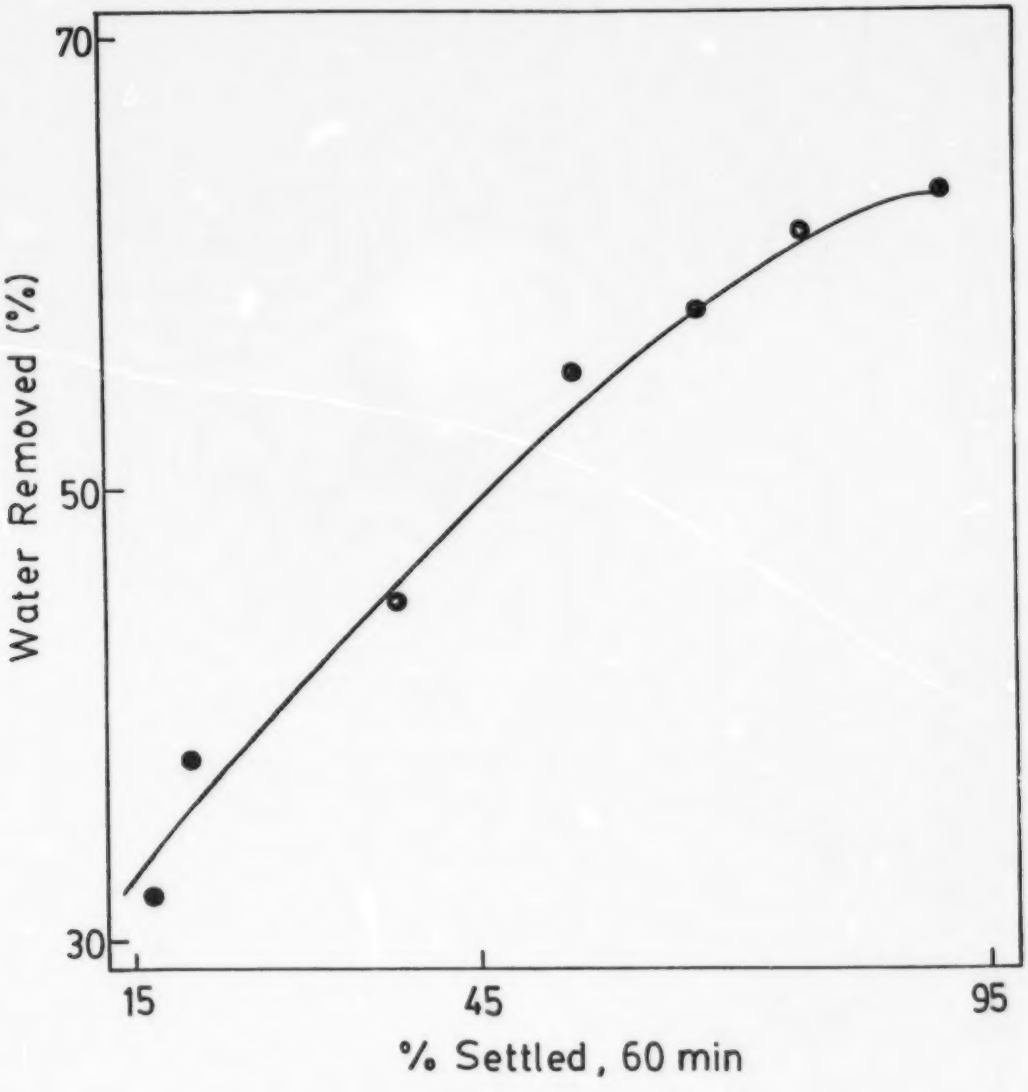


Table 5.3. The Effect of the Cationic Polyelectrolyte, Praestol 411K, on Mechanical De-Watering of Barrington Peat and on Peat Particle Settling

Ratio of Praestol 411K to Dry Peat (wt/wt)	Amount of Water Removed (kg H_2O/kg dry peat)	Water Removed (%)	Moisture Content of Pressed Peat (%)	% Sett 60 min
Control	2.45	33.7	82.9	22.8
0.004	2.53	34.8	82.6	27.4
0.010	3.04	41.8	80.9	30.5
0.016	3.38	46.4	79.6	33.3
0.026	3.29	45.2	80.0	50.0
0.040	3.47	47.7	79.2	69.0
0.52	3.41	46.8	79.5	70.8
0.056	3.43	47.1	79.4	93.8
0.063	2.82	38.7	81.7	70.8

Total Water Content = 7.28 kg H_2O/kg dry peat
% Water Content = 87.9%

Figure 5.7. Enhancement of water removal from peat with Praestol 411K. Water removal (▲) and particle settling after 60 min (●) versus the ratio of Praestol 411K to dry peat in the sample (wt/wt).

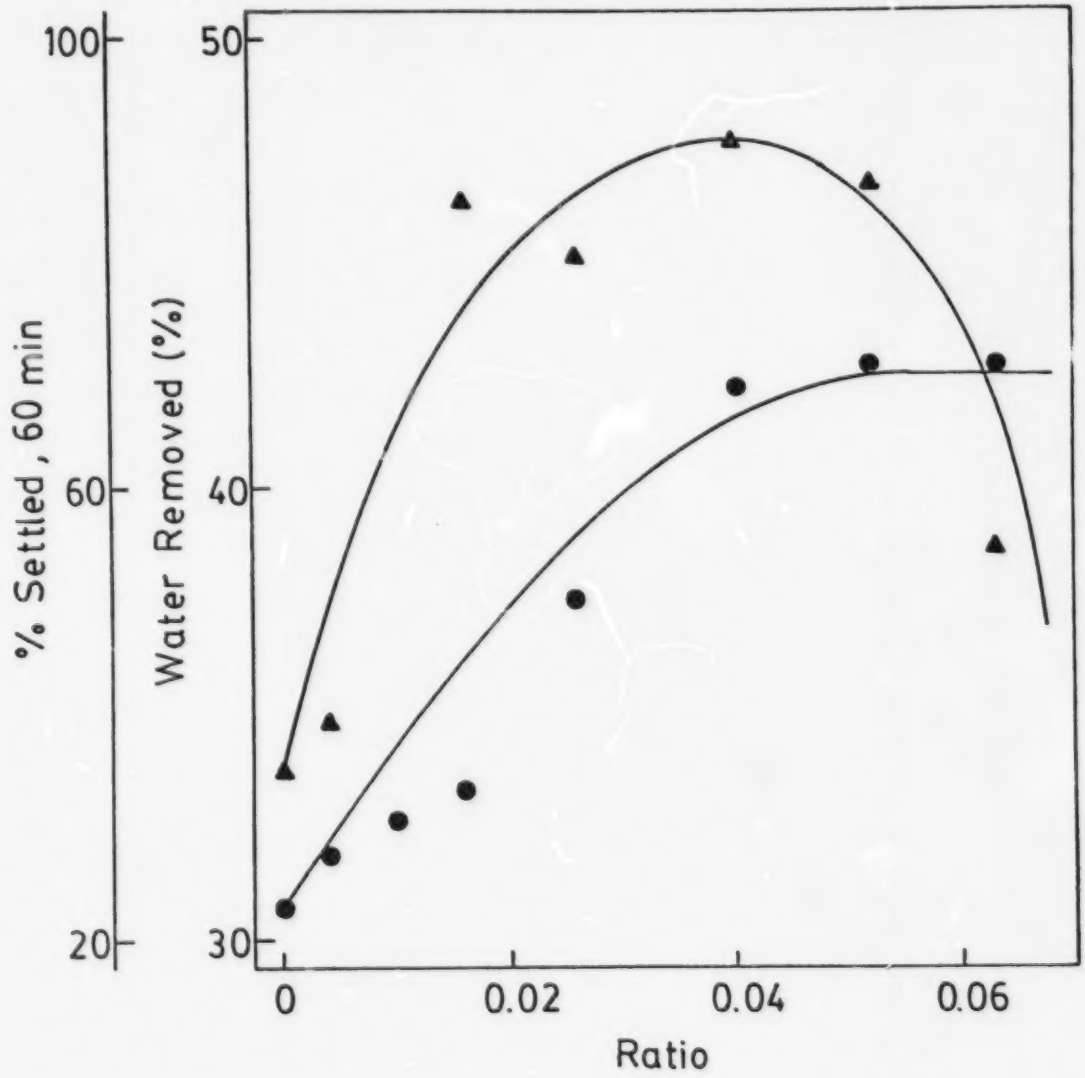
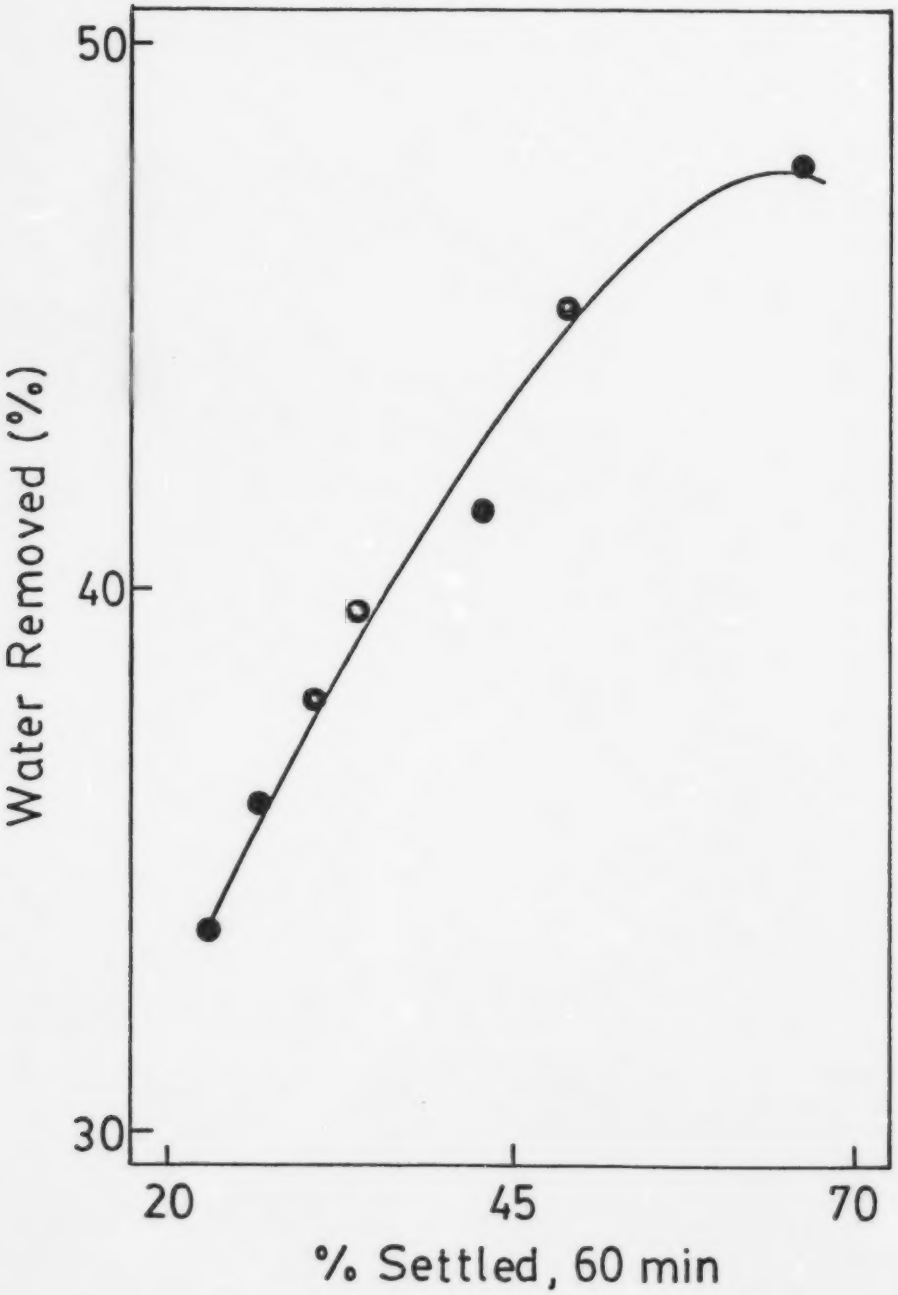


Figure 5.8. Enhancement of water removal from peat with Praestol 411K. Water removal versus particle settling after 60 min.



flocculation are the mechanisms by which water removal is enhanced. The polyelectrolytes would initially cause a charge neutralization of the negative peat particles causing coagulation and thereby freeing more water to be removed by mechanical pressing. Secondly, flocculation may occur as the polyelectrolytes associate with several charged peat particles to form larger clumps.

5.2. Inorganic Salts

If the improved water removal by polyelectrolytes was simply a charge meutralization phenomenon then inorganic salts such as, NH_4Cl and others should be just as effective as the polyelectrolytes. This would not necessarily happen if flocculation was important and the particle settling rates should be lower since the particles will be smaller if flocculation does not occur. Four salts were studied, three inorganic salts, NH_4Cl, $FeCl_3$ and $AlCl_3$, and one quaternary ammonium salt, dodecyltrimethylammonium bromide (DTAB), which also has surfactant properties.

The results (Table 5.4.) for NH_4Cl show that this salt was not as effective in enhancing mechanical water removal as chitosan or Praestol 444K when compared on the basis of number of charges. The maximum water removal was 55.2%.
It did, however, remove a significant amount compared to the control (55.2% compared to 38.2% for the control). This gives further evidence to the charge neutralization of the peat particles. The settling rate of the particles was much lower than for the polyelectrolytes. Figures 5.9. and 5.10. indicate that although

Table 5.4. The Effect of NH_4Cl on Mechanical De-Watering of Barrington Peat and on Peat Particle Settling

Ratio of NH_4Cl to Dry Peat (wt/wt)	Number of Charged Sites ($X10^{20}$)	Amount of Water Removed (kg H_2O/kg dry peat)	Water Removed (%)	Moisture Content of Pressed Peat (%)
Control	-	2.78	38.2	81.8
0.004	1.13	3.80	52.2	77.7
0.010	2.25	4.02	55.2	76.5
0.017	4.50	3.80	52.2	77.7
0.030	7.87	3.85	52.8	77.4
0.043	11.3	3.80	52.2	77.7
0.048	14.6	3.77	51.8	77.8

Total Water Content = 7.28 kg H_2O/kg dry peat
% Water Content = 87.9%

Figure 5.9. Enhancement of water removal from peat with NH_4Cl. Water removal (▲) and particle settling after 60 min (●) versus the ratio of NH_4Cl to dry peat in the sample (wt/wt).

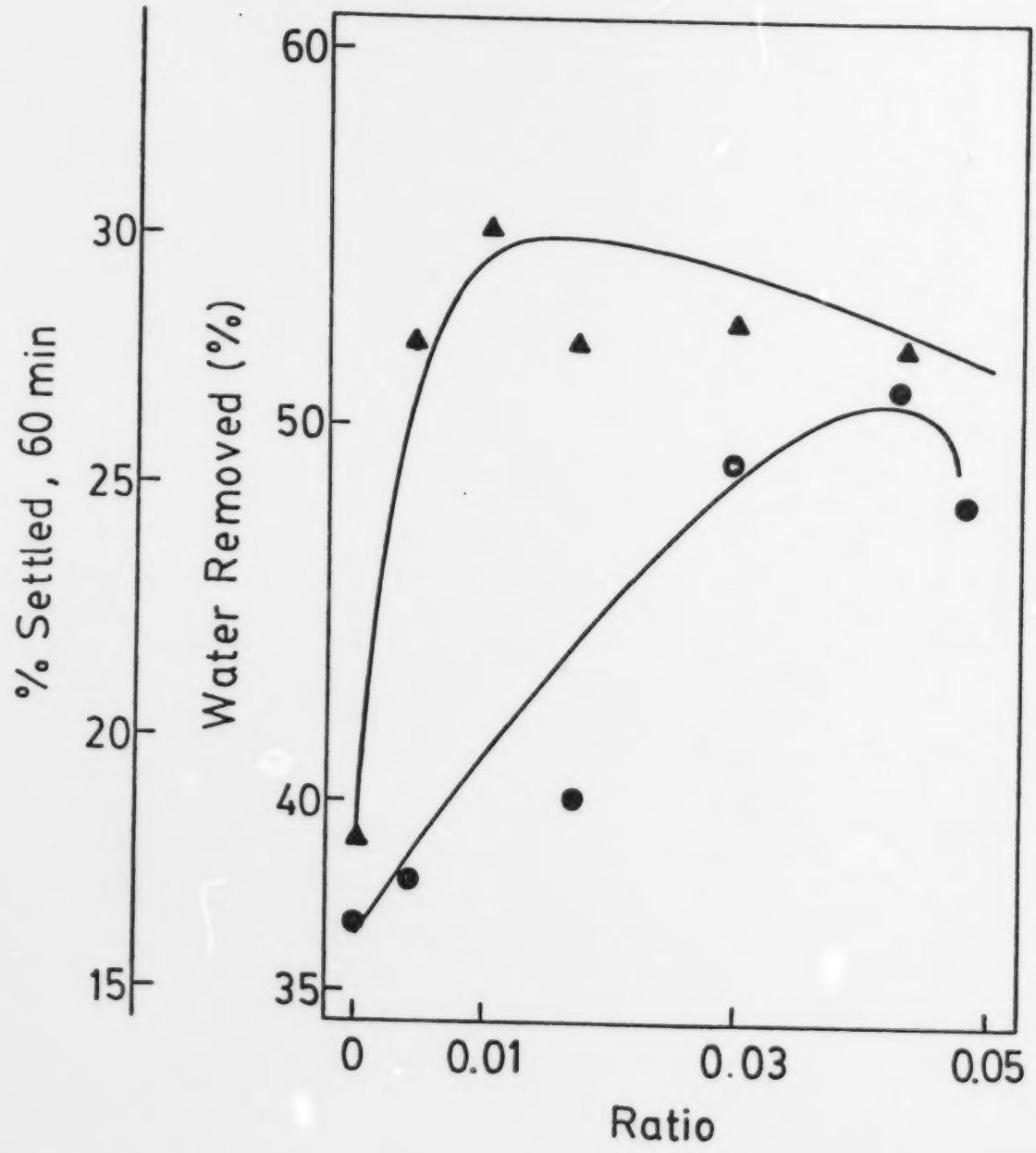


Figure 5.10. Enhancement of water removal from peat with NH_4Cl. Water removal (▲) and particle settling after 60 min (●) versus the number of charged sites contained in NH_4Cl added to the peat sample.

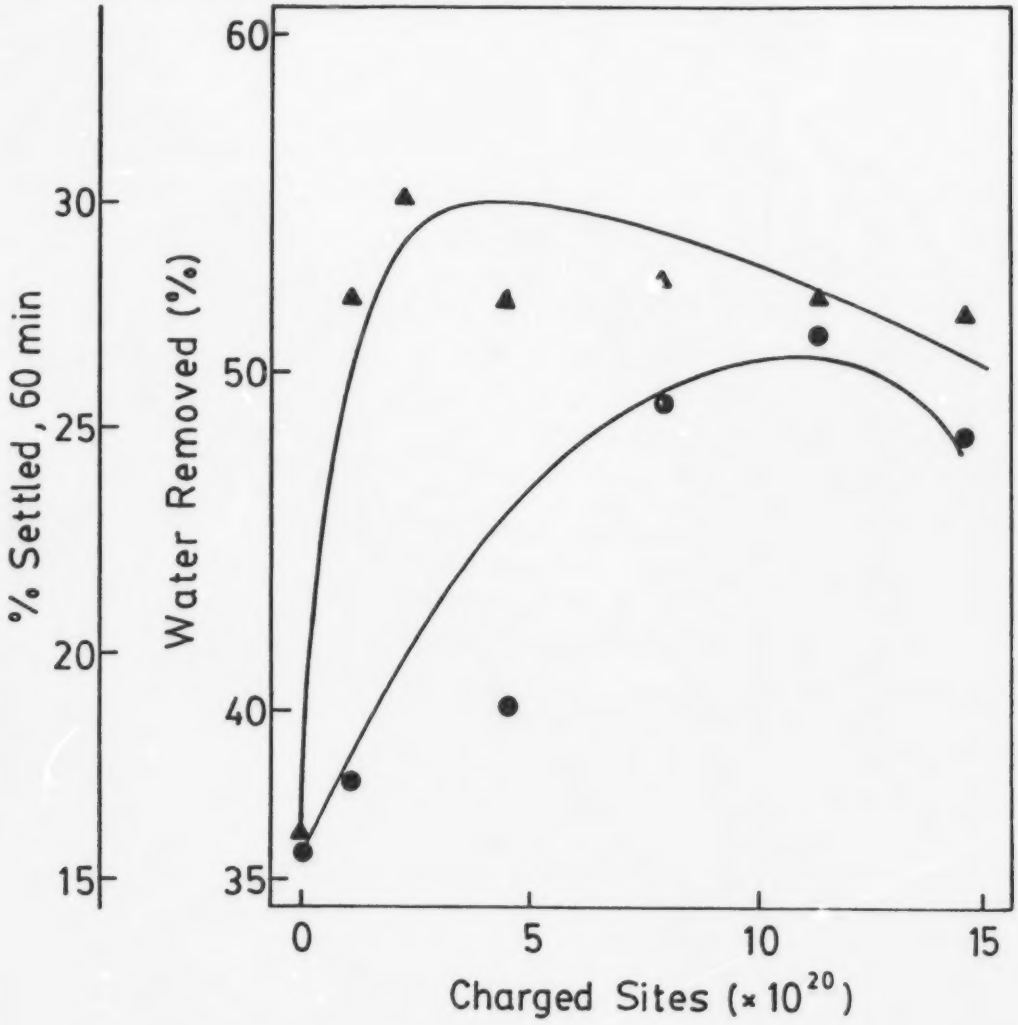
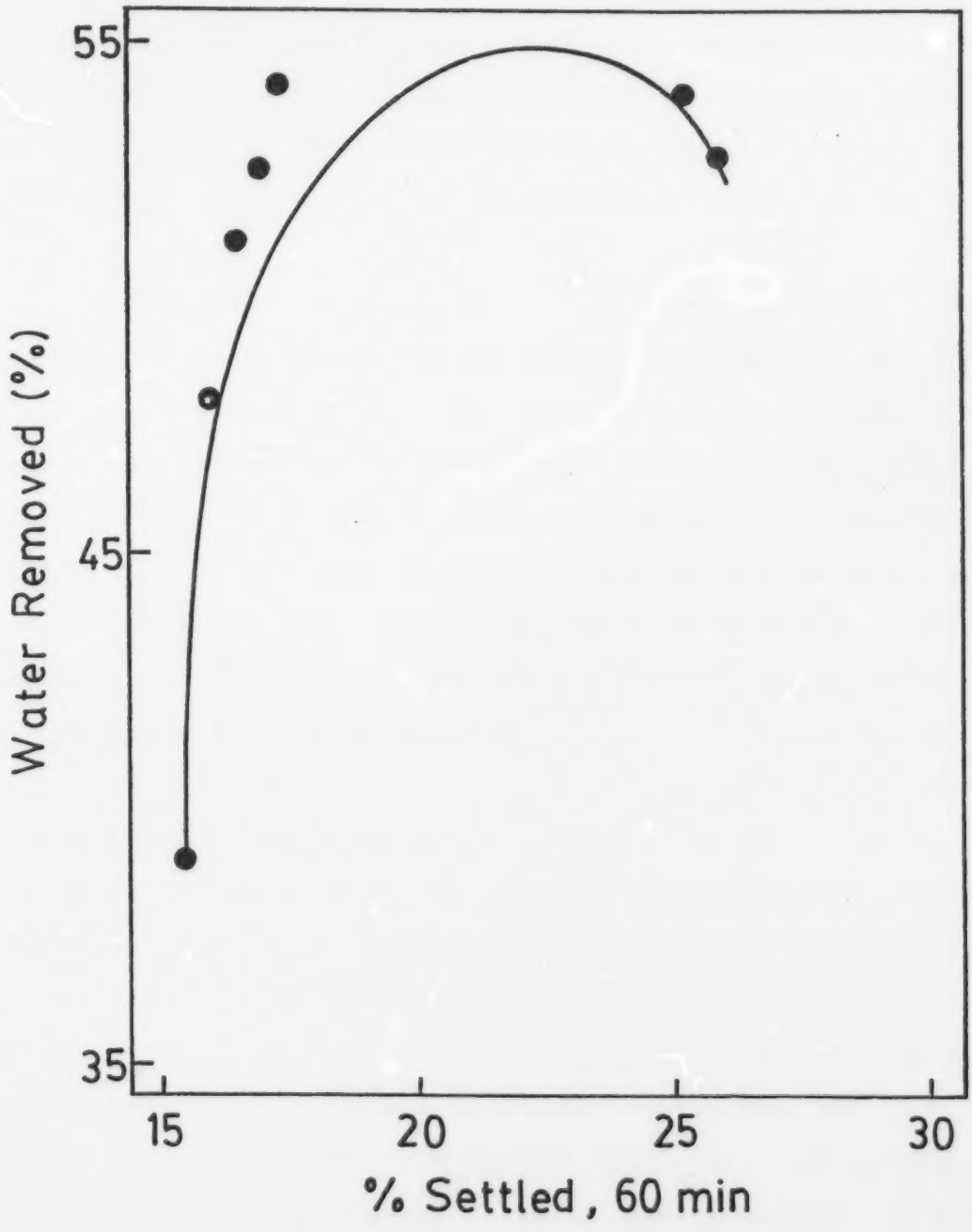


Figure 5.11. Enhancement of water removal from peat with NH_4Cl. Water removal versus particle settling after 60 min.



the settling rate is low, it does increase and then decrease similar to the polyelectrolytes. However, the increase-decrease pattern of water removal and particle settling occur at much different concentrations. They do not occur at similar concentrations as is the case with the polyelectrolytes. The correlation between water removal and particle settling is not very strong (Figure 5.11.).

DTAB was effective in enhancing water removal (Table 5.5). The maximum water removal was 68.9%. The particle settling was higher than for the inorganic salts. The DTAB removed more water than any other molecule studied, although chitosan and Praestol 444K were only a few percentage points lower. Again, DTAB showed an excellent correlation between water removal and particle settling (Figures 5.12. and 5.13.). Each parameter increased and then decreased at almost the same concentration of DTAB. Also, when these two parameters are examined together (Figure 5.14.), their graph is linear.

This compound is acting as a coagulating agent but its surfactant properties may also be implicated in the de-watering as it is more effective than the other compounds tested. The first report demonstrated that even neutral and anionic surfactants aided de-watering.

The results for $FeCl_3$ also show that water removal is enhanced (Table 5.6.). The maximum water removal was 68.1%. This result was impressive but it was attained at a much higher concentration of the additive than for previously studied molecules. The settling rate was also high. This is not surprising as $FeCl_3$

Table 5.5. The Effect of Dodecyltrimethylammonium Bromide (DTAB) on Mechanical De-Watering of Barrington Peat and on Peat Particle Settling

Ratio of DTAB to Dry Peat (wt/wt)	Number of Charged Sites ($X10^{20}$)	Amount of Water Removed (kg H_2O/kg dry peat)	Water Removed (%)	Moisture Content of Pressed Peat (%)
Control	-	2.41	33.1	82.9
0.004	0.195	3.15	43.3	80.5
0.018	0.781	3.98	54.7	76.7
0.030	1.37	4.26	58.5	75.1
0.042	1.95	4.65	63.9	72.5
0.055	2.54	5.01	68.8	69.4
0.060	2.93	4.31	59.2	74.8
0.068	3.32	4.36	59.9	74.5

Total Water Content = 7.28 kg H_2O/kg dry peat
% Water Content = 87.9%

Figure 5.12. Enhancement of water removal from peat with DTAB. Water removal (▲) and particle settling after 60 min (●) versus the ratio of ΔTAB to dry peat in the sample (wt/wt).

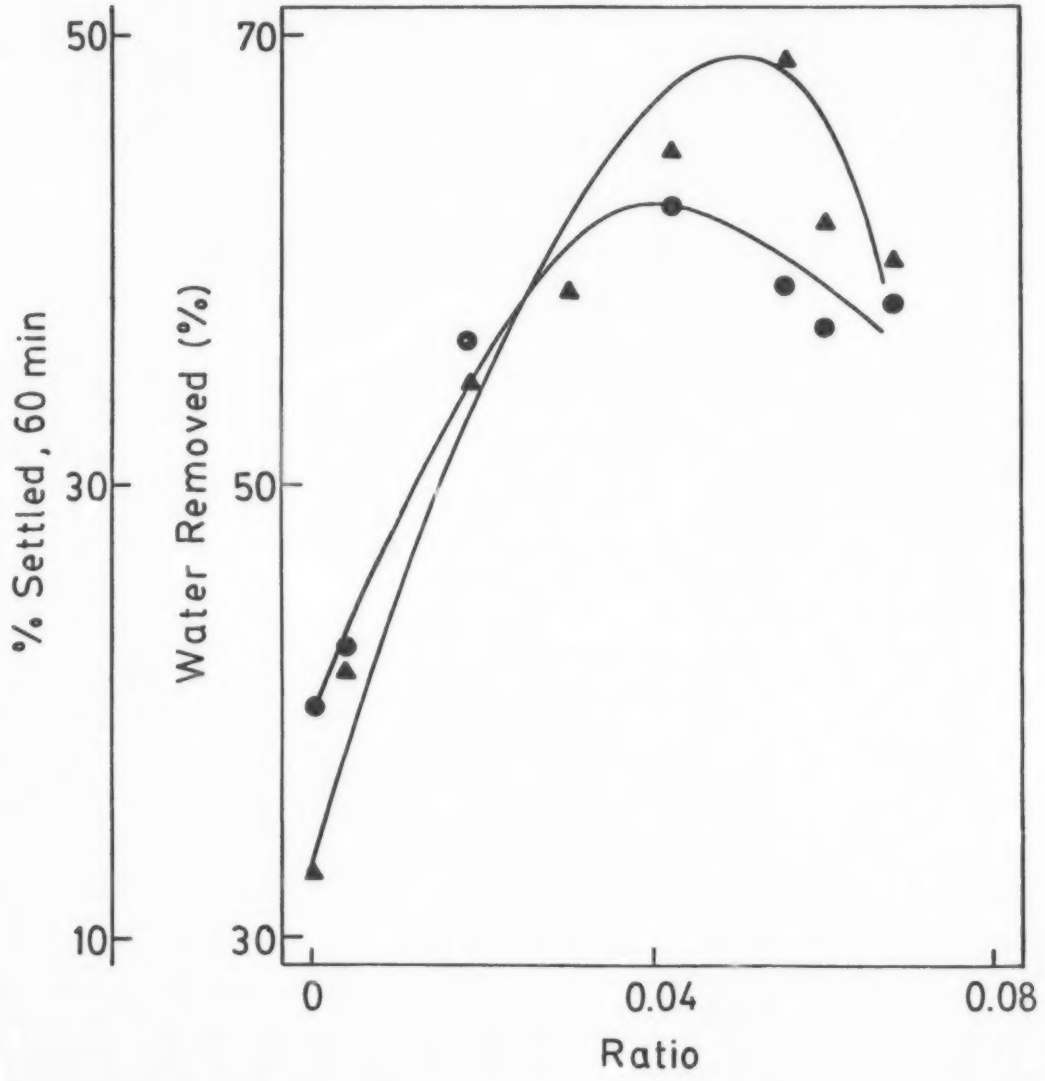


Figure 5.13. Enhancement of water removal from peat with DTAB. Water removal (▲) and particle settling after 60 min (●) versus the number of charged sites contained in DTAB added to the peat sample.

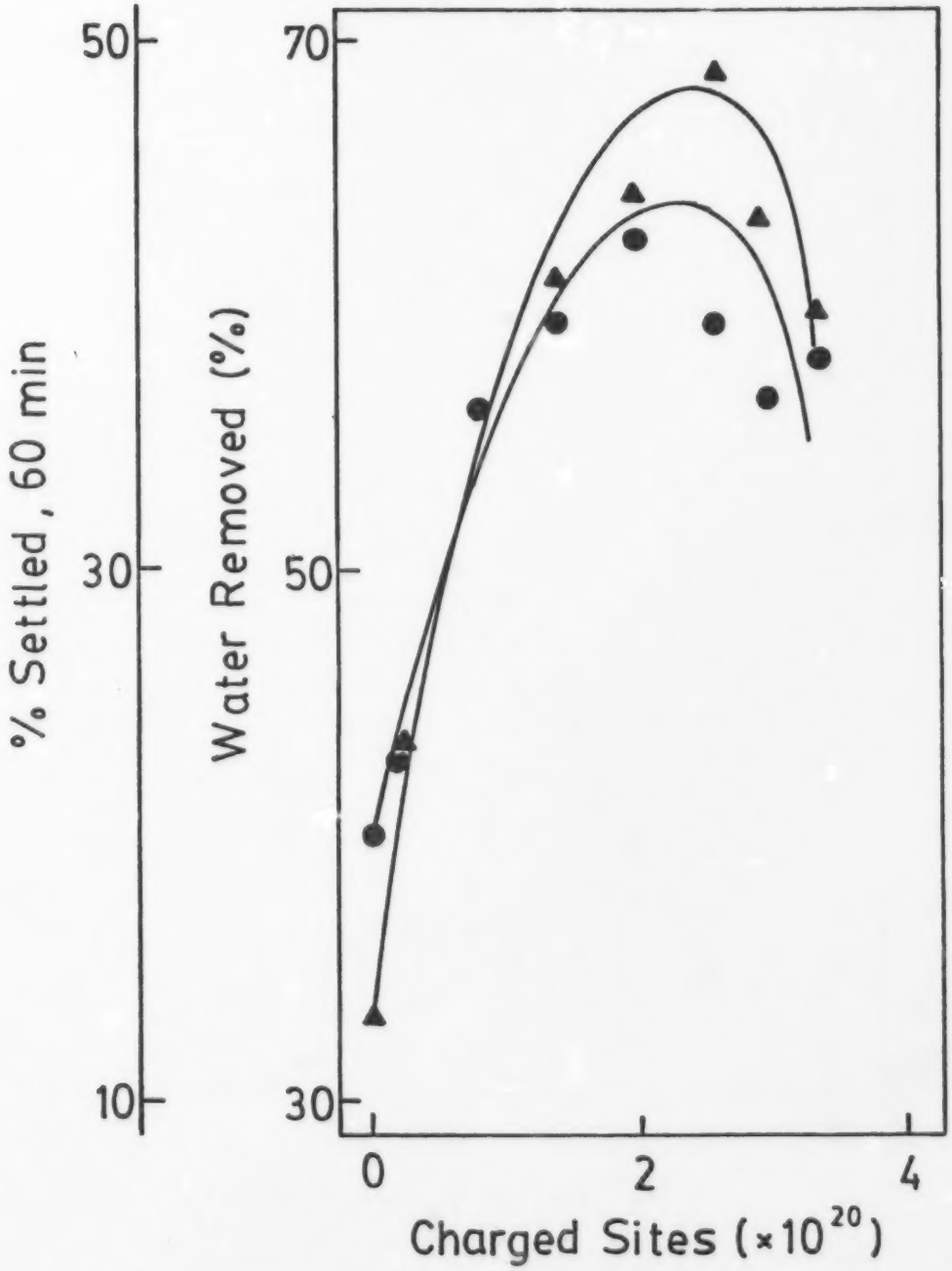
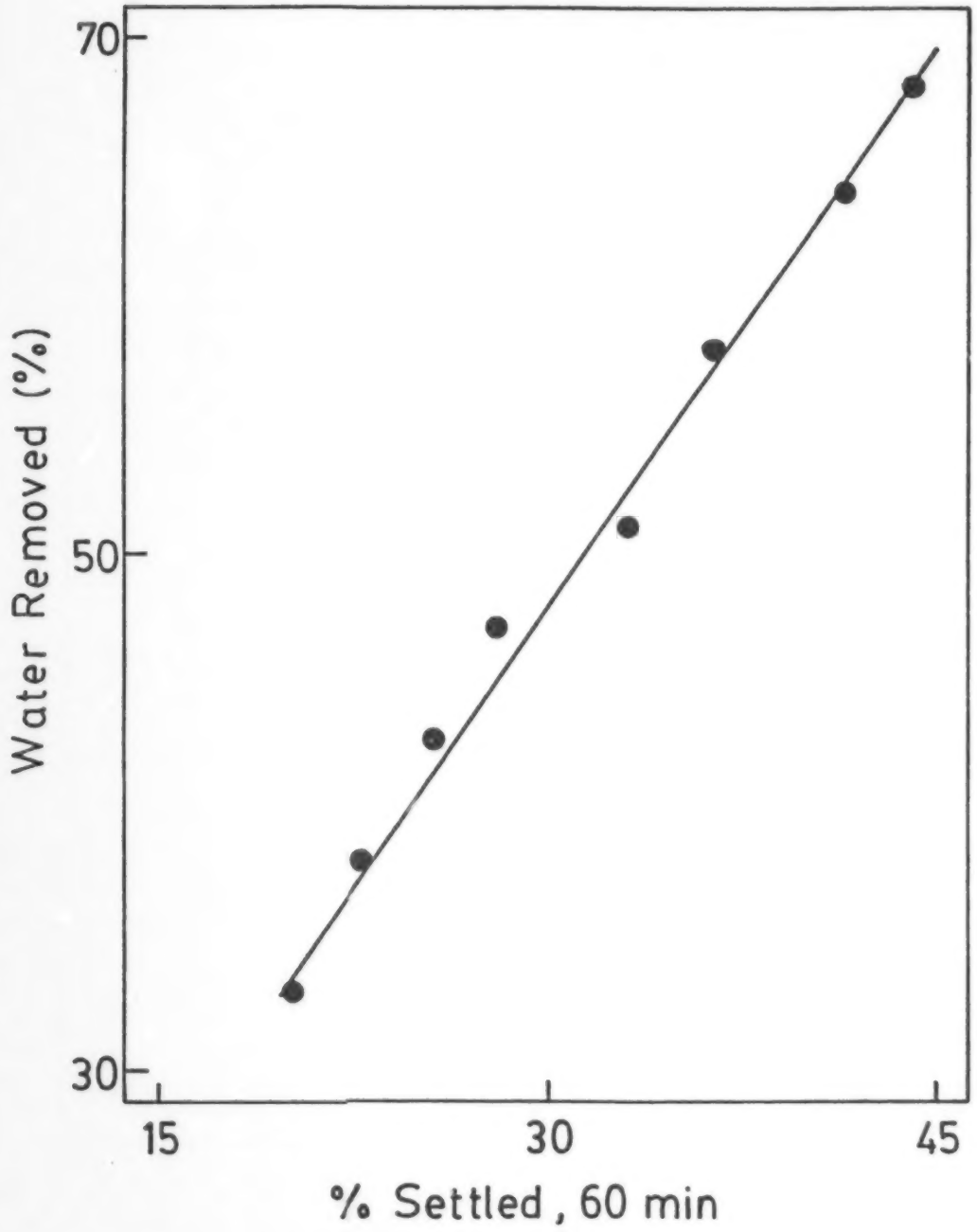


Figure 5.14. Enhancement of water removal from peat with DTAB.
Water removal versus particle settling after 60 min.



is a well known coagulating agent for waste water treatment[2]. Figures 5.15. and 5.16. are similar to the previous molecules studied, that is, they show an initial increase and then a decrease in both water removal and particle settling, with each occurring at about the same concentration. The graphical comparison of water removal and particle settling (Figure 5.17.) shows a very good correlation between them suggesting, again, that coagulation is an important part of the water removal mechanism.

Finally, $AlCl_3$ was investigated (Table 5.7.). The water removal was enhanced (maximum of 63.6%) and the particle settling was also excellent. However, Figures 5.18. and 5.19. indicate that these parameters do not have their maximums at the same additive concentrations. There is not the same correlation between as in previous examples as can be seen by Figure 5.20. which does not approach linearity. The results (Table 5.7.) do show, however, that $AlCl_3$ is very effective in enhancing mechanical water removal.

This study demonstrates that addition of cationic species to peat does improve the mechanical water removal. Also, the chloride salt of chitosan, which can be produced microbially, is as effective as any chemical compound in the investigation. It is worth noting that while the metal salts such as $FeCl_3$ are relatively cheap, they would not be appropriate for de-watering fuel grade peat, as they would significantly increase the ash content.

Table 5.6. The Effect of $FeCl_3$ on Mechanical De-Watering of Barrington Peat and on Peat Particle Settling

Ratio of $FeCl_3$ to Dry Peat (wt/wt)	Number of Charged Sites ($X10^{20}$)	Amount of Water Removed (kg H_2O/kg dry peat)	Water Removed (%)	Moisture Content of Pressed Peat (%)
Control	-	2.64	36.3	82.3
0.004	0.370	3.78	51.9	77.8
0.018	1.48	4.25	58.4	75.2
0.032	2.59	4.32	59.3	74.8
0.043	3.71	4.58	62.9	72.9
0.058	4.82	4.58	62.9	73.0
0.062	5.56	4.96	68.1	69.9
0.070	6.67	4.62	63.5	72.7

Total Water Content = 7.28 kg H_2O/kg dry peat
% Water Content = 87.9%

Figure 5.15. Enhancement of water removal from peat with $FeCl_3$. Water removal (▲) and particle settling after 60 min (●) versus the ratio of $FeCl_3$ to dry peat in the sample (wt/wt).

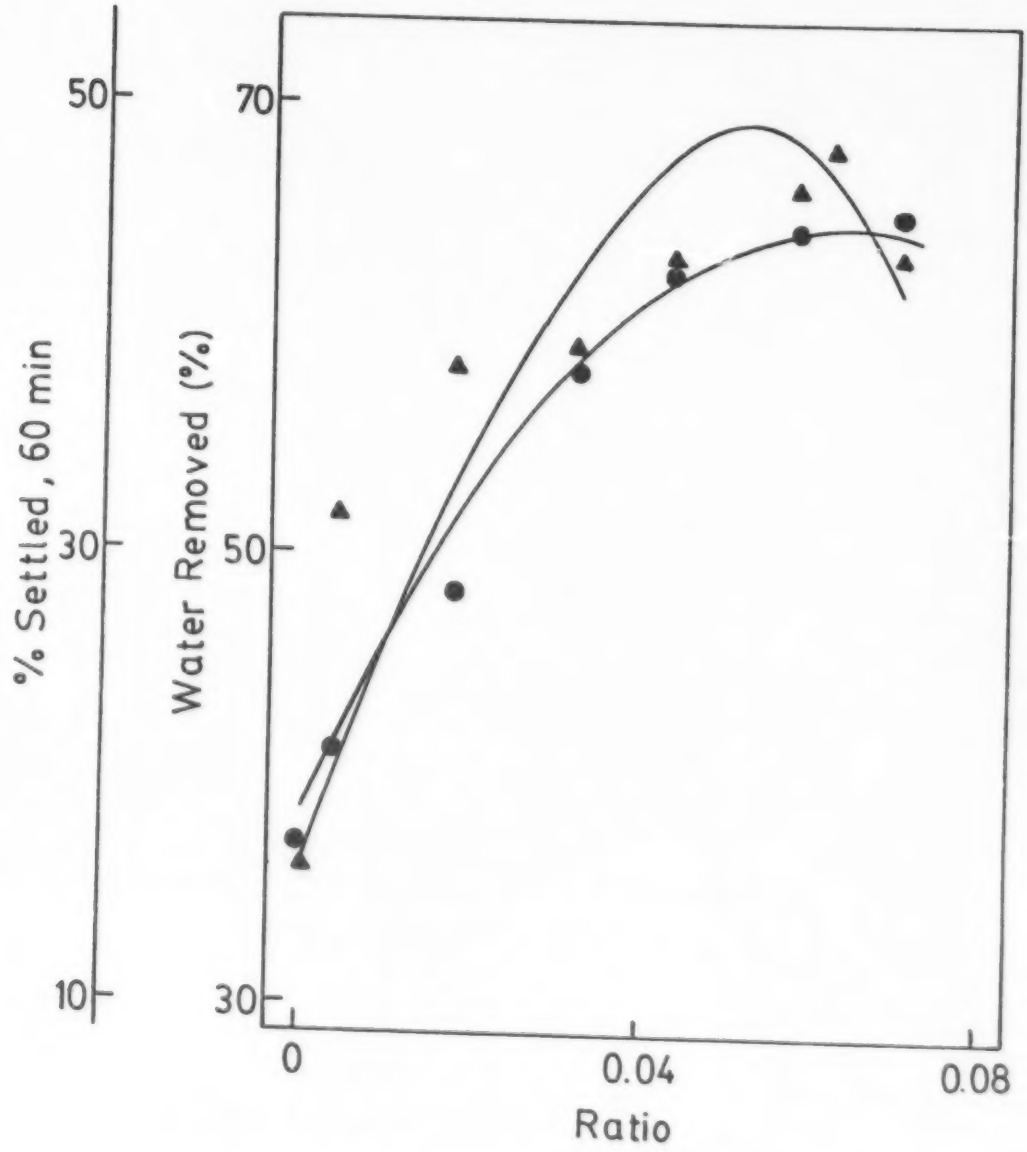


Figure 5.16. Enhancement of water removal from peat with $FeCl_3$. Water removal (▲) and particle settling after 60 min (●) versus the number of charged sites in $FeCl_3$ added to the peat sample.

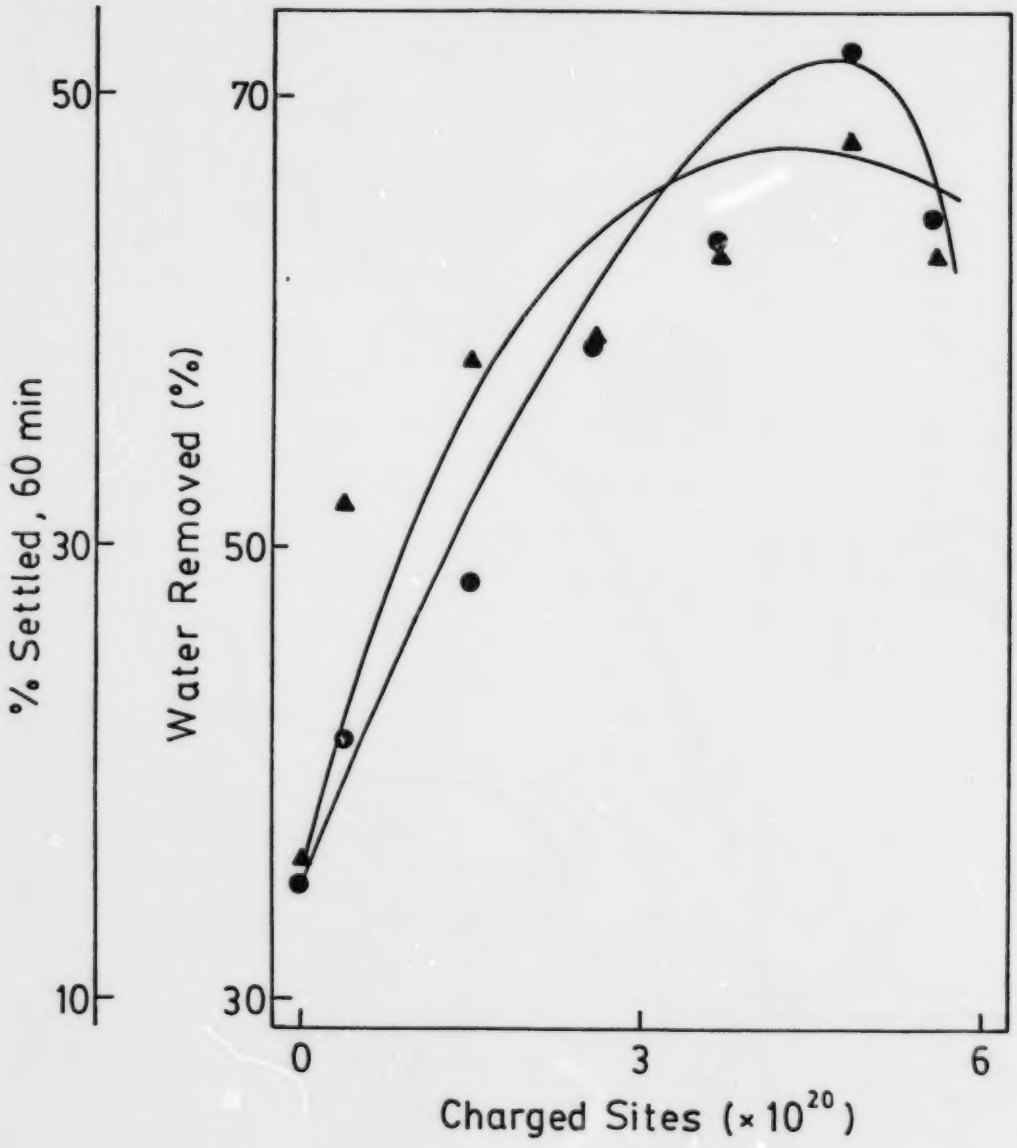


Figure 5.17. Enhancement of water removal from peat with $FeCl_3$. Water removal versus particle settling after 60 min.

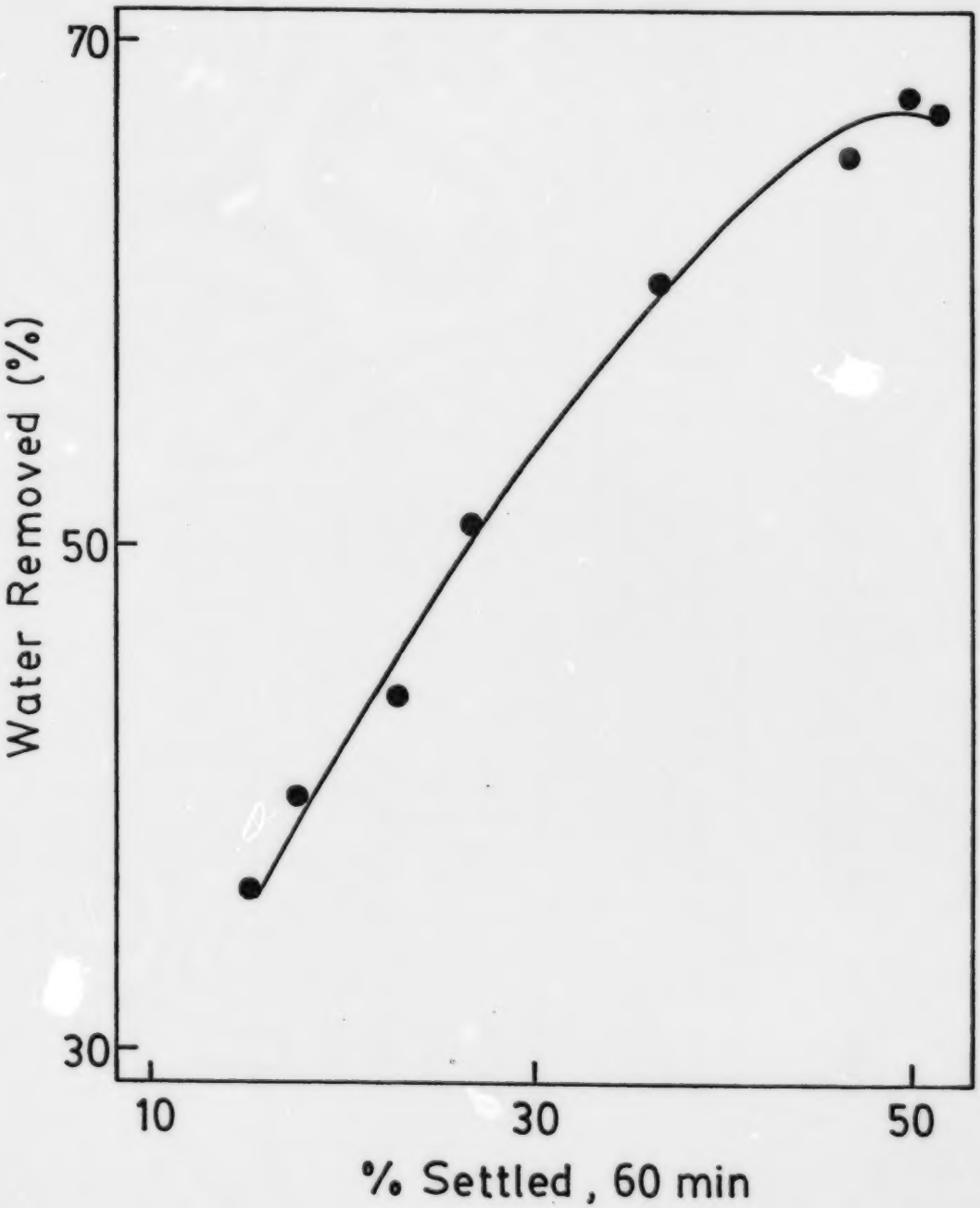


Table 5.7. The Effect of $AlCl_3$ on Mechanical De-Watering of Barrington Peat and on Peat Particle Settling

Ratio of $AlCl_3$ to Dry Peat (wt/wt)	Number of Charged Sites ($X10^{20}$)	Amount of Water Removed (kg H_2O/kg dry peat)	Water Removed (%)	Moisture Content of Pressed Peat (%)
Control	-	2.62	36.0	82.3
0.005	0.451	4.44	61.0	74.0
0.018	1.80	4.63	63.6	72.6
0.032	3.16	4.59	63.0	72.9
0.048	4.51	4.47	61.4	73.8
0.054	5.86	4.31	59.2	74.8

Total Water Content = 7.28 kg H_2O/kg dry peat
% Water Content = 87.9%

Figure 5.18. Enhancement of water removal from peat with AlCl . Water removal (▲) and particle settling after 60 min (●) versus the ratio of AlCl to dry peat in the sample (wt/wt).

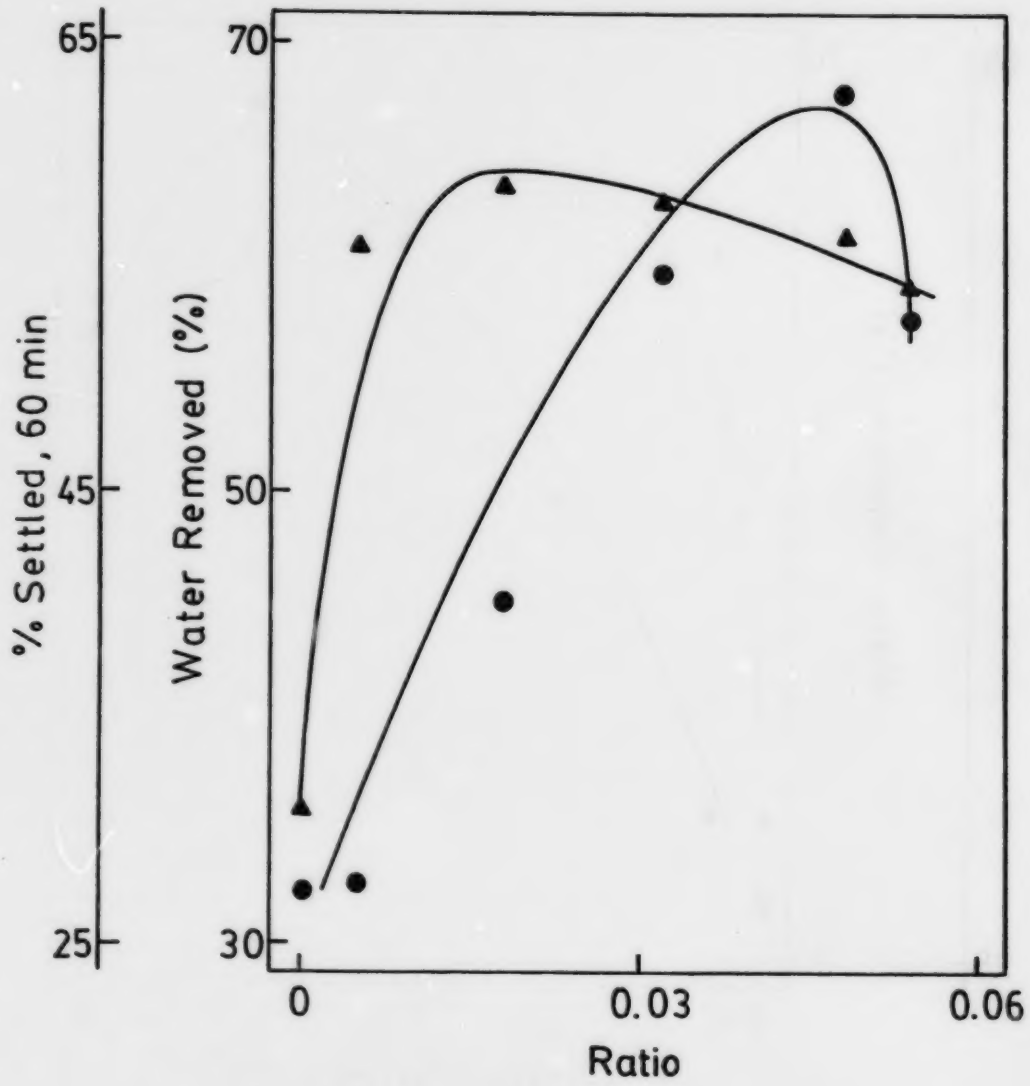


Figure 5.19. Enhancement of water removal from peat with AlCl . Water removal from peat with AlCl . Water removal (▲) and particle settling after 60 min (●) versus the number of charged sites contained in AlCl added to the peat sample.

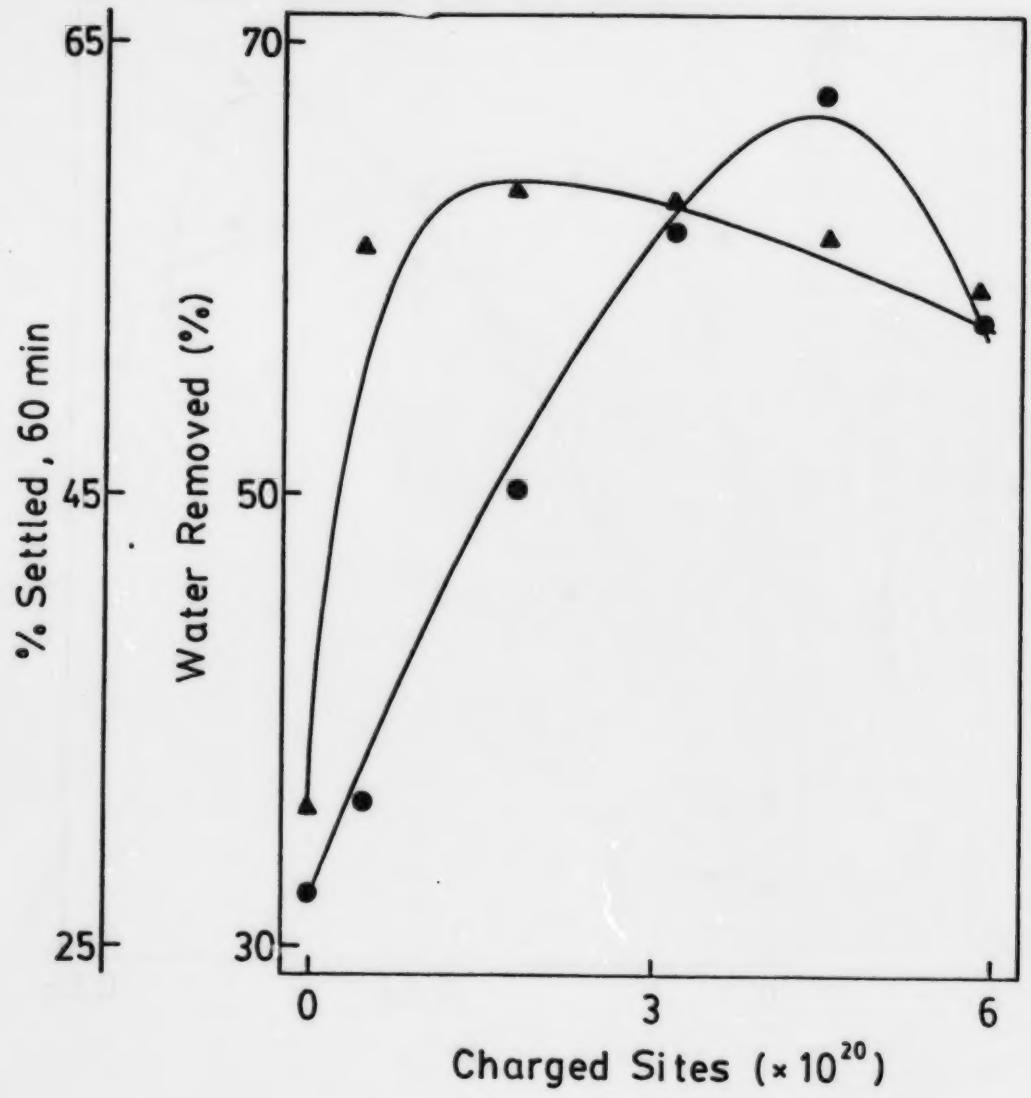
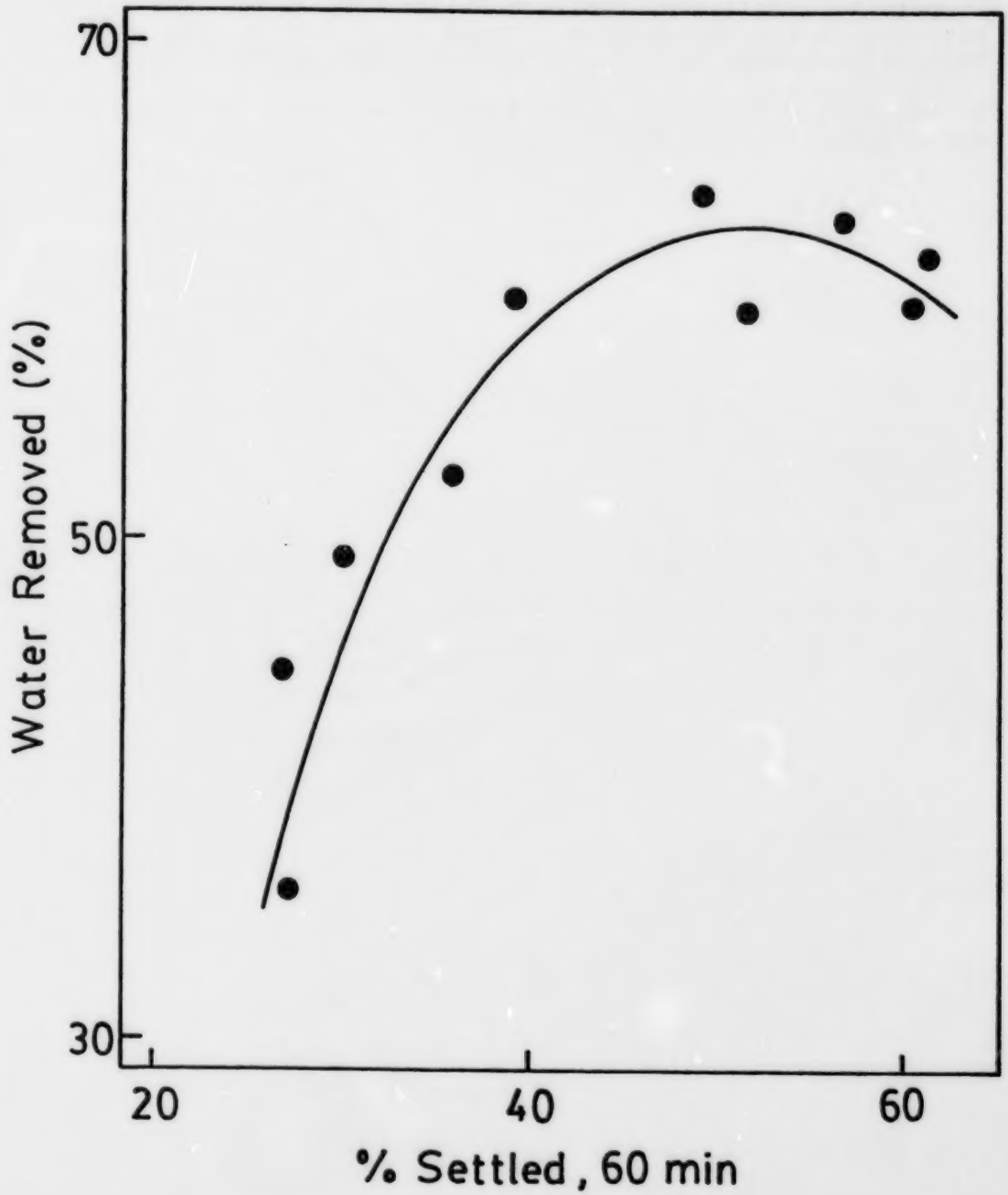


Figure 5.20. Enhancement of water removal from peat with $AlCl_3$. Water removal versus particle settling after 60 min.



5.3. REFERENCES

1. Cooper, D.G. Mulligan, C.N. and Pillon D.W. 1984. The Use of Microbes in the De-Watering of Fuel Grade Peat. Final Report. National Research Council Contract No. DSS ISU83-00030.

2. Baker, M.N. 1981. "The Quest for Pure Water". American Water Works Association. Denver.

CHAPTER 6

ENHANCED MECHANICAL DE-WATERING OF PEAT USING CHEMICAL AND THERMAL PRETREATMENT

6.1. Characterizing the Heating Apparatus

All heat pretreatment experiments were performed in a simple Parr 4501 two-liter pressure vessel. The pressure vessel is equipped with stirrer, cooling coils and valves for injecting and venting gases. The vessel is heated by placing it into a heating jacket which is controlled by a rheostat. The temperature inside the vessel is monitored by a dial thermometer whose stem is placed into a thermowell which is immersed in the peat. With this equipment it was first necessary to establish procedures for heating peat to desired temperatures. After trial and error experimentation the rheostat was calibrated. The data is shown in Table 6.1.

For each procedure shown in Table 6.1. the heat up time required for the peat, which is initially at room temperature, to reach the final temperature is approximately 30 minutes. After the final temperature is reached the peat may be held at this temperature or cooled off immediately. In the first experiments run with the calibrated apparatus the peat was held at the final temperature for 15 minutes. The heating curves shown in figures 6.1 and 6.2 provide a percise picture of the heating process. For example, in Figure 6.1. the peat is heated to 176° C in 30 minutes, point A, then held at this temperature for 15 minutes, point B, and finally cooled quickly back to room temperature.

TABLE 6.1. CALIBRATION OF PARR PRESSURE REACTOR

FINAL TEMPERATURE	PROCEDURE
125° C	120 for 30 mins. cut to 45% after one minute in jacket.
100° C	120 for 20 mins. cut to 15% after one minute in jacket.
75° C	110 for 15 mins. cut to zero and place in jacket.
52° C	100 for 10 mins. cut to zero and place in jacket.
153° C	120 for 1 hr. cut to 30% after 3 min. in jacket.
177° C	120 for 1 hr. cut to 50% after 8 mins. in jacket.
197° C	120 for 80 mins. cut to 70% after 12 mins. in jacket.

FIGURE 6.1. Temperature of peat in the vessel during thermal pretreatment vs. time. The figure shows the heat up region, the first 30 mins., and the 15 minute holding time.

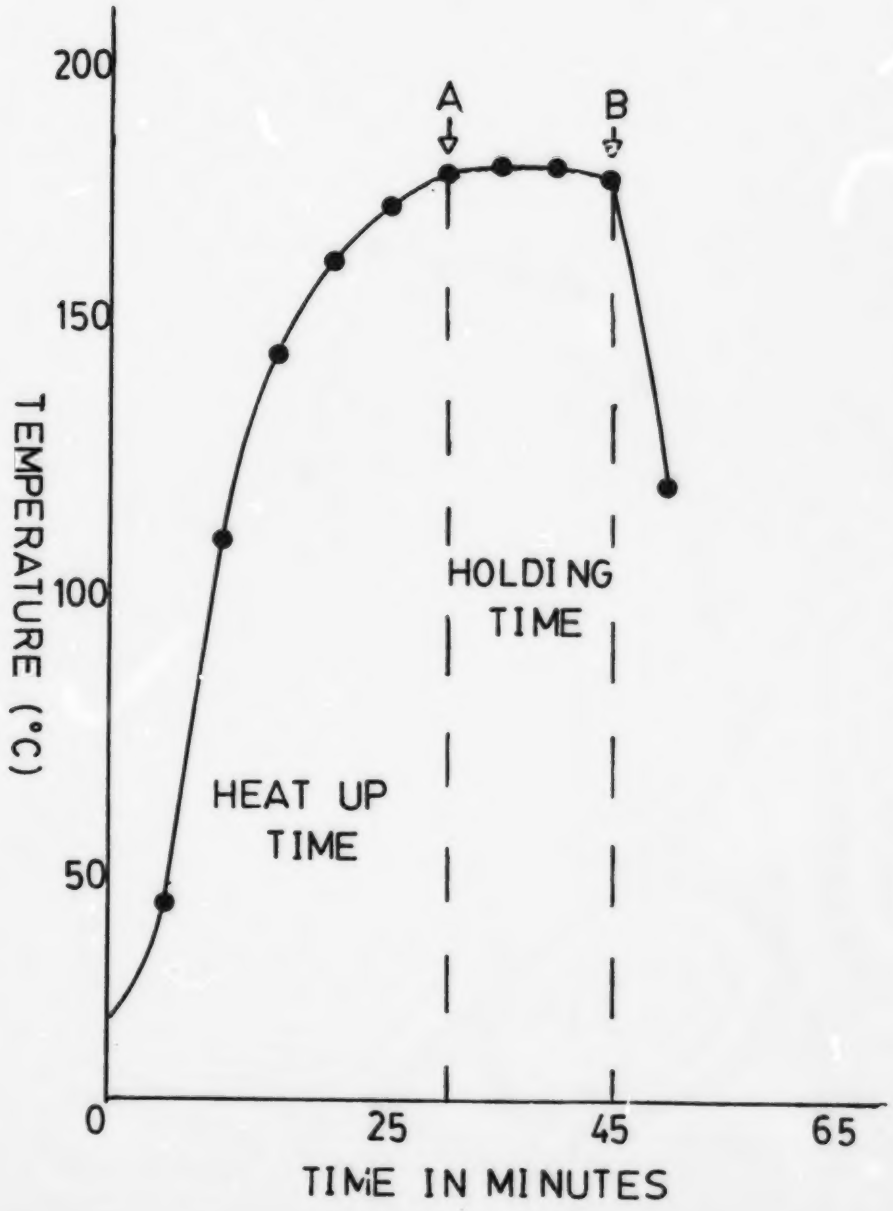
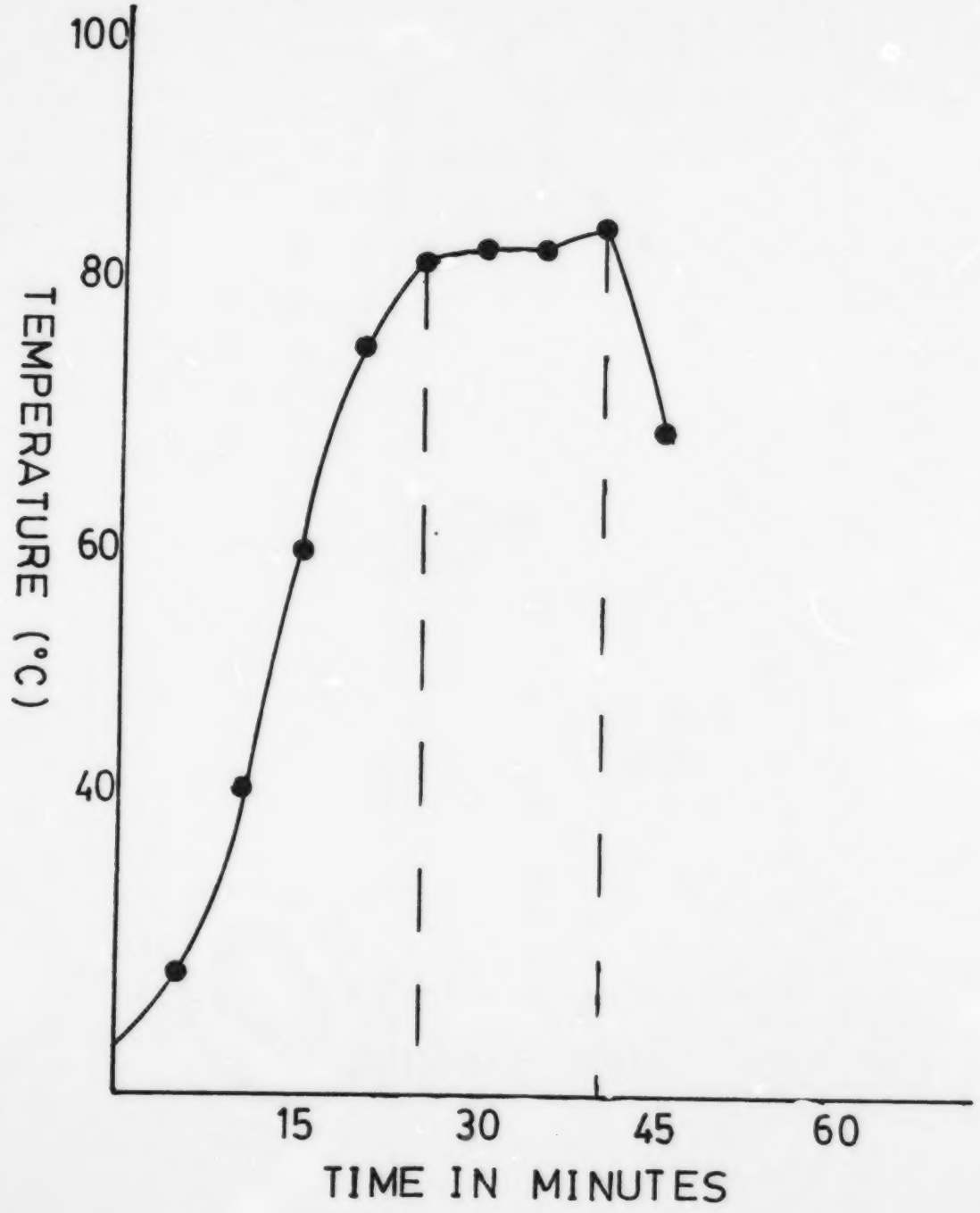


FIGURE 6.2. Temperature of peat in vessel during thermal pre-treatment vs. time. The figure shows the heat up region, the first 28 minutes, and the 15 minute holding time.



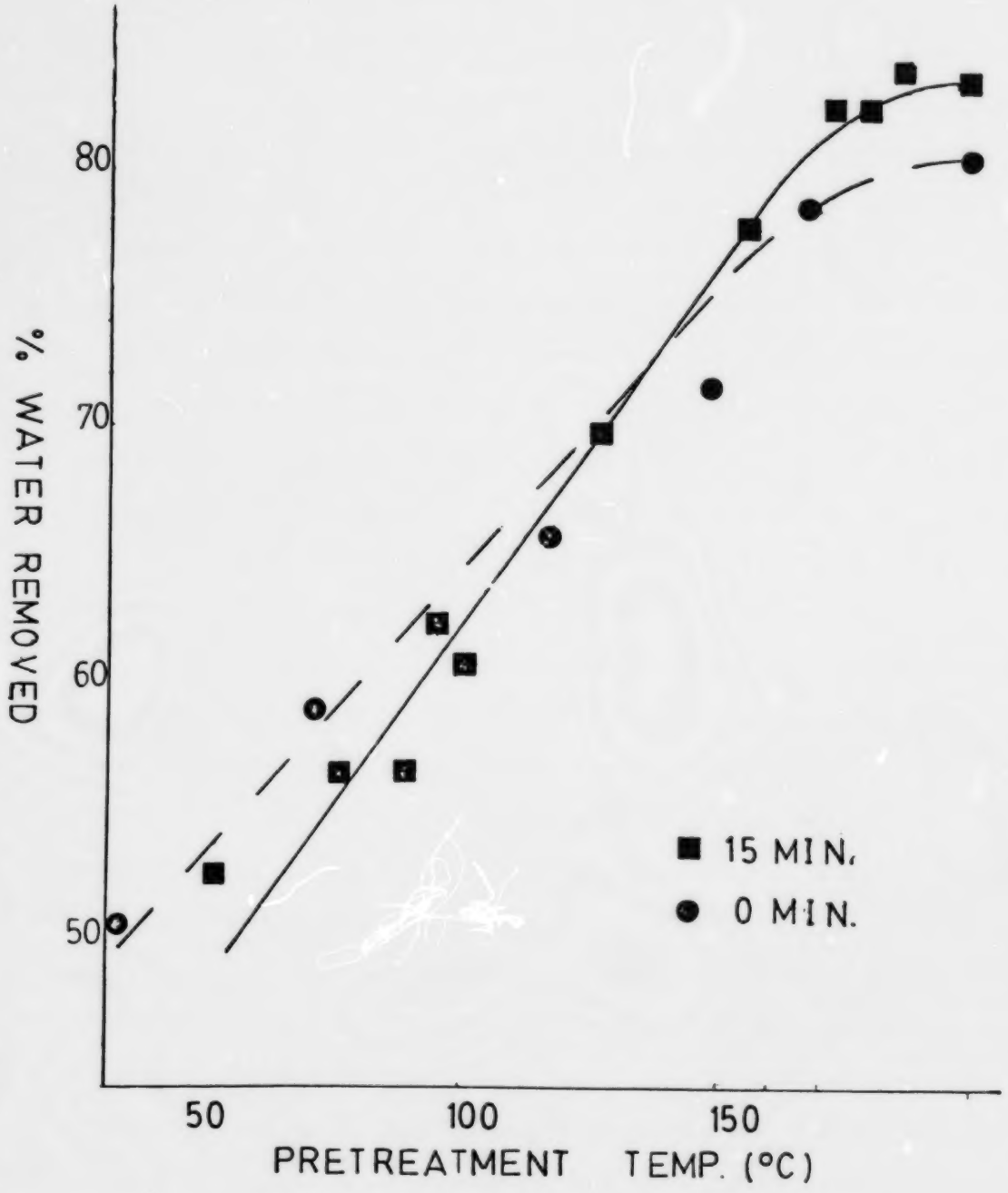
6.2. FIFTEEN MINUTE AND ZERO HOLDING TIME EXPERIMENTS:

Eleven heat pretreatment runs were done with a 15 minute holding time. Each run had a heat up curve similar to Figure 6.1. After heat pretreatment, 3 samples at each temperature were cooled, pressed and the amount of water removed was calculated. The average amount of water removed by pressing for each temperature tested is plotted in Figure 6.3. As expected, as the temperature increases the amount of water removed by pressing increases. However, even relatively low temperatures were effective. For example heating the peat to just 75° C improved the amount of water removed during pressing from 50.2% the control value, to 56.1%, a 12% increase. This improvement continues to increase steadily with temperature up to 175° C, where the effect begins to level off, and about 85% of the water is removed.

Also shown in Figure 6.3 are the results of six heat pretreatment runs done with zero holding time. Again there is significant improvement in the amount of water removed at only 68° C, where 58.6% is removed a 17% increase over the control.

The two curves in Figure 6.3 fall very close to each other. Up to 140° C the 15 minute residence curve lies below the zero minute curve, at this point they cross and beyond 140° C the 15 minute residence time runs are more effective. The difference between the two curves, however, is within the range of experimental error. Therefore at low temperatures and short residence times the final temperature is the more sensitive parameter in determining heat effects on the de-watering of peat. This con-

FIGURE 6.3. The percent water removed after thermal pretreatment vs. the temperature. The results from both 15 minute (■) and zero minute (●) holding time experiments are plotted. The heat up time is 30 minutes.



clusion has been reached by others doing slightly higher temperature heating[1,2]. The majority of experiments which followed were done with zero holding time.

6.3. EFFECT OF HEAT UP RATE

After studying two different residence times the effect of a change in the heat up rate was examined. The residence time parameter was varied using a 30 minute heat up time as shown in Figures 6.1 and 6.2. Figure 6.4 shows a heating curve for a run in which the heat up time is 15 minutes, the residence time is zero, and the final temperature is 150° C. Four runs were done with 15 minute heat up time; they are plotted in Figure 6.5.

The curve drawn through the squares in Figure 6.5 shows the relationship between percent water removed during pressing and the pretreatment temperature, when the heat up time is 30 minutes and the residence time is zero. The curve drawn through the circles differs only in that the heat up time is 15 minutes. The 15 minute heat up time data lies consistently below the 30 minute heat up time data. The difference between the curves at any temperature is about 6% water removed. Therefore, two conclusions can be made: (1) a change in heat up time in this temperature range has a significant effect on the amount of water removed during pressing and (2) the difference in the percent of water removed for the two heat up times is nearly constant at all the temperatures studied.

FIGURE 6.4. The temperature of peat in the vessel during thermal pretreatment vs. time. The heat up time is 14 minutes and the residence time is zero.

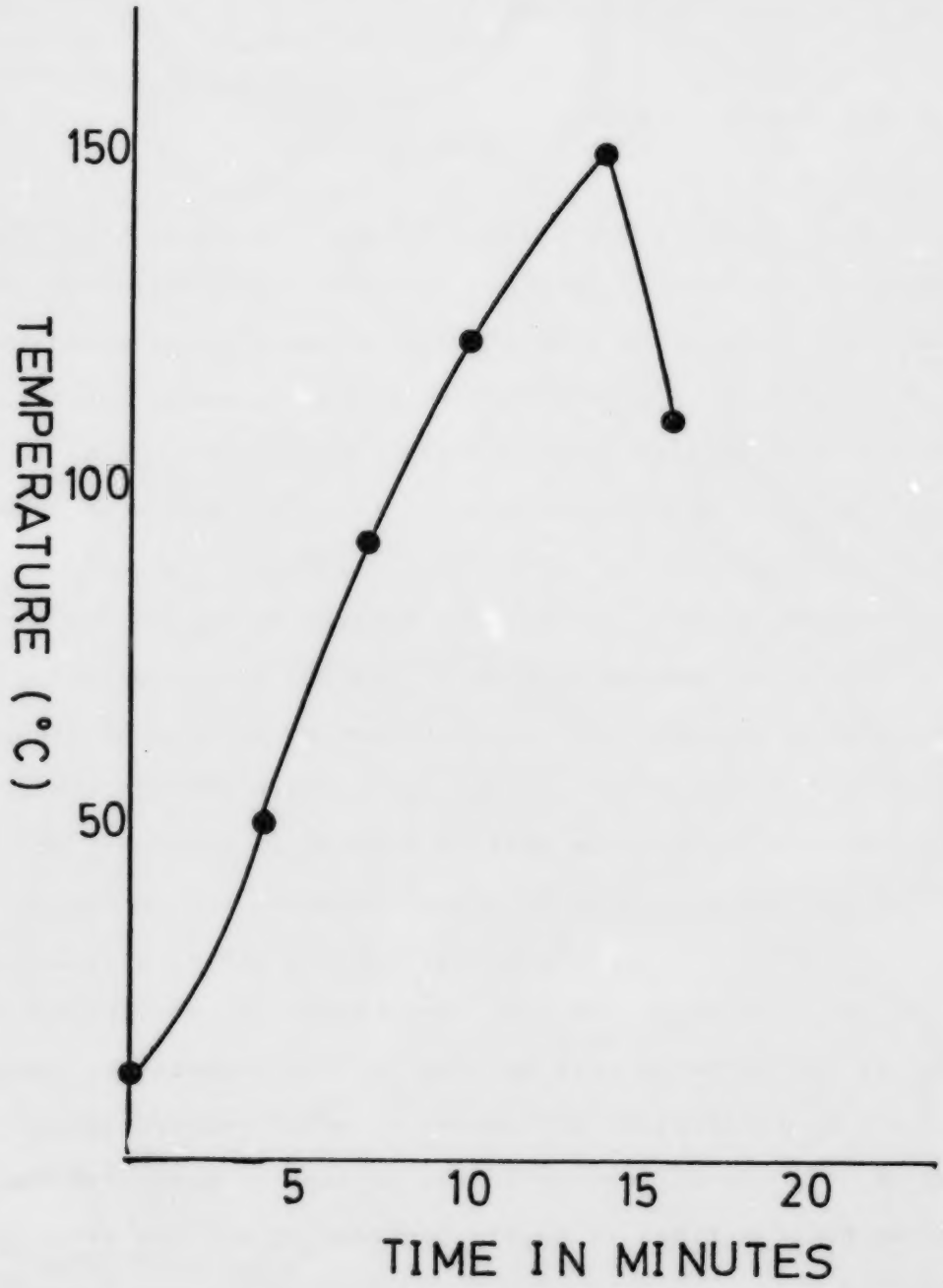
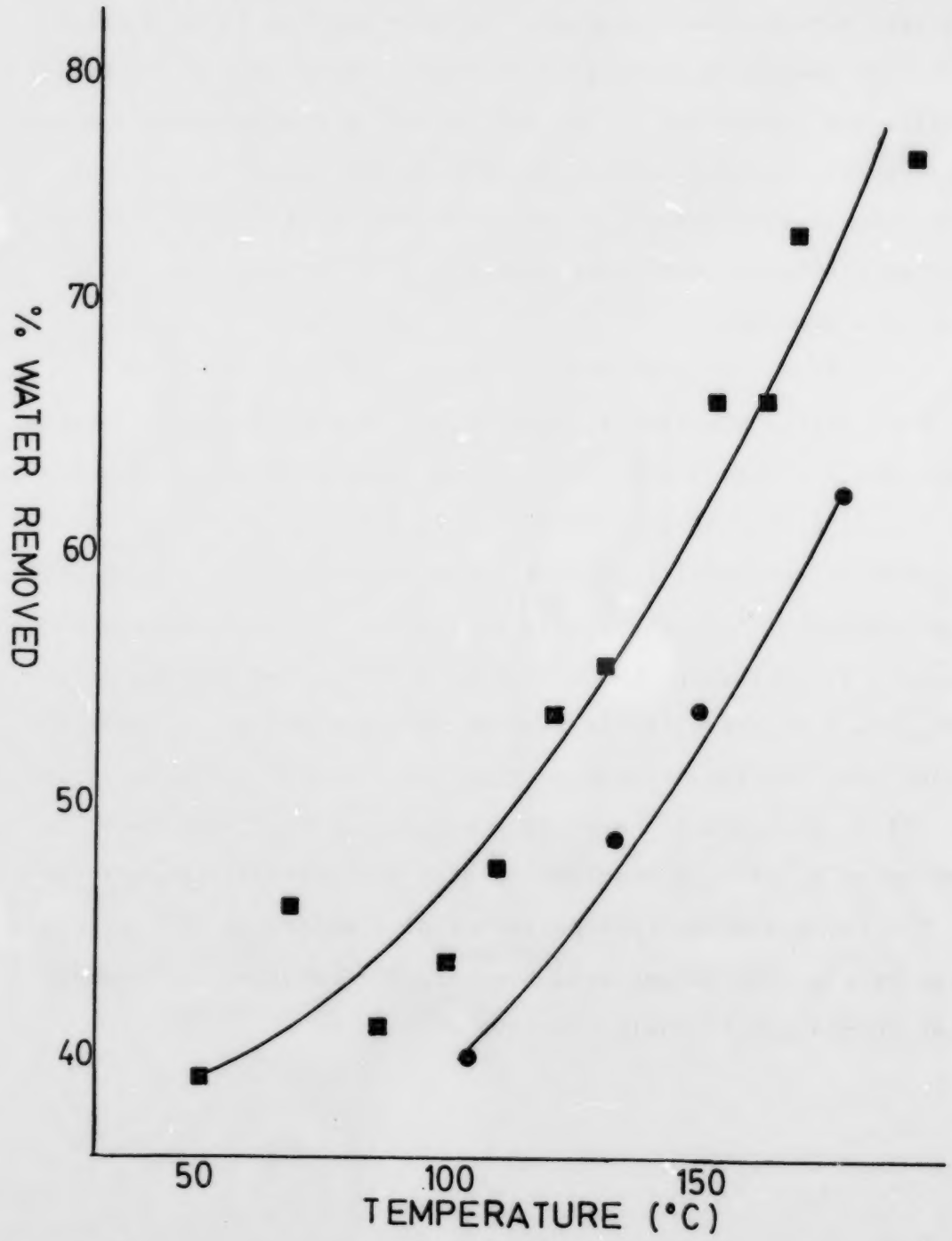


FIGURE 6.5. The percent water removed after thermal pretreatment vs. temperature. The results for both 30 minute (■) and 15 minute (●) heat up rates are shown, the holding time is zero minutes.

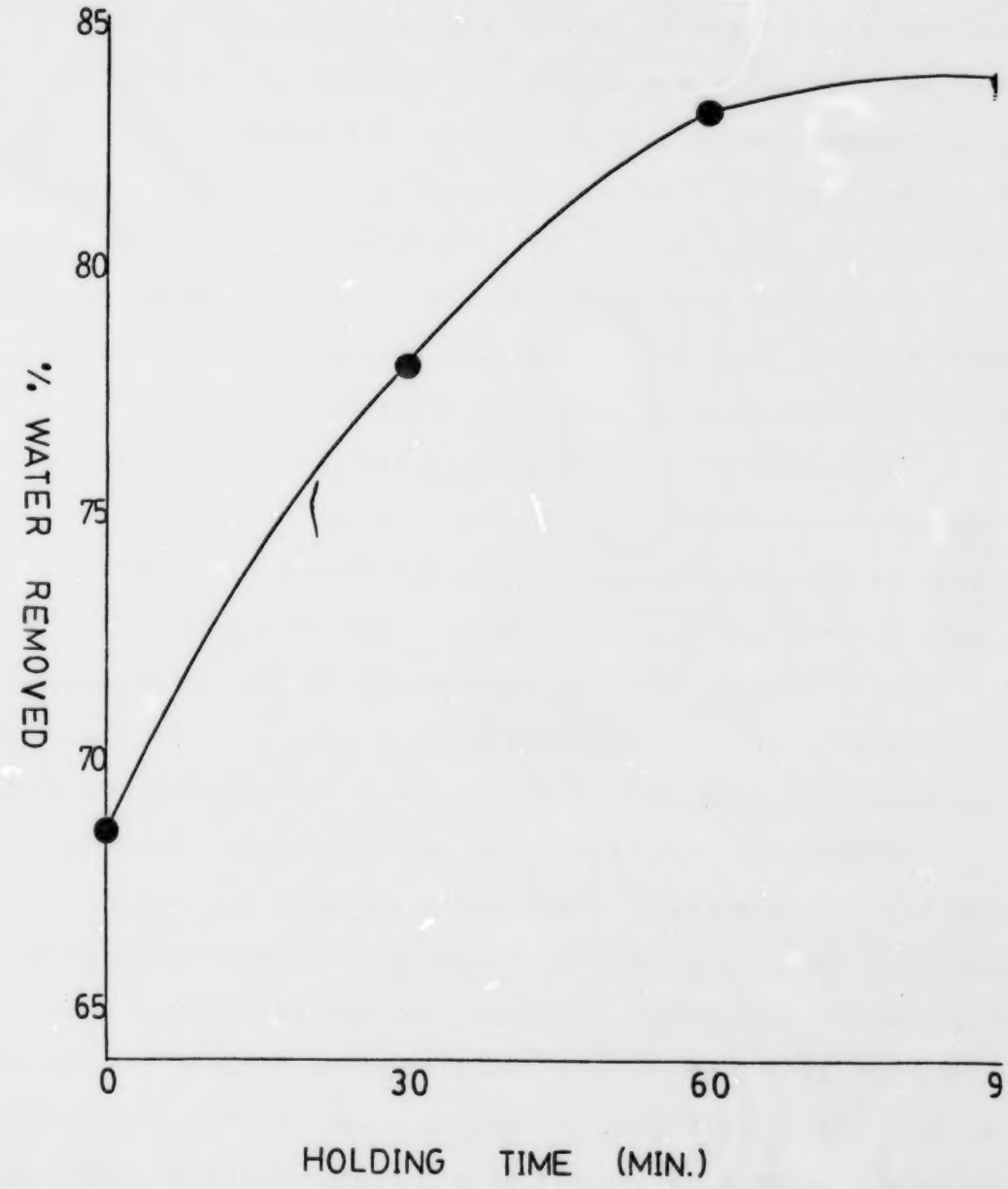


6.4. RESIDENCE TIME EXPERIMENTS

In section 6.2 data on two residence times, 15 minutes and zero minutes, is discussed. In that section it is concluded that both residence times produce heat treated peat with similar de-watering properties in the 50° to 200° C pretreatment temperature range. Although almost 20 data points were obtained the pretreatment temperature is the principal variable. Therefore, a further residence time experiment was done in which the temperature is a constant.

Four runs were done in which the residence times were 0 minutes, thirty minutes, 60 minutes and 90 minutes. The maximum temperature reached, also the holding temperature, in each case is 165° C. The data is plotted in Figure 6.6. It shows that an increase in residence time does cause an increase in the amount of water removed. Note the y-axis in Figure 7.3 has been expanded in Figure 6.6. The improvement is significant at 60 minutes holding time, 83.2% of the water is removed during pressing, a 16.7% increase over the zero residence time run. However, the curve levels off at this point and at 90 minutes only 0.6% more water is removed or 83.9%. In conclusion, at a pretreatment temperature of 165 ° C the residence time parameter does determine heat treated peats de-watering properties, however, the marginal improvement after 60 minutes is insignificant.

FIGURE 6.6. The percent water removed after thermal pretreatment vs. the holding time. The pretreatment temperature is 165° C in each experiment. The heat up time is 30 minutes.



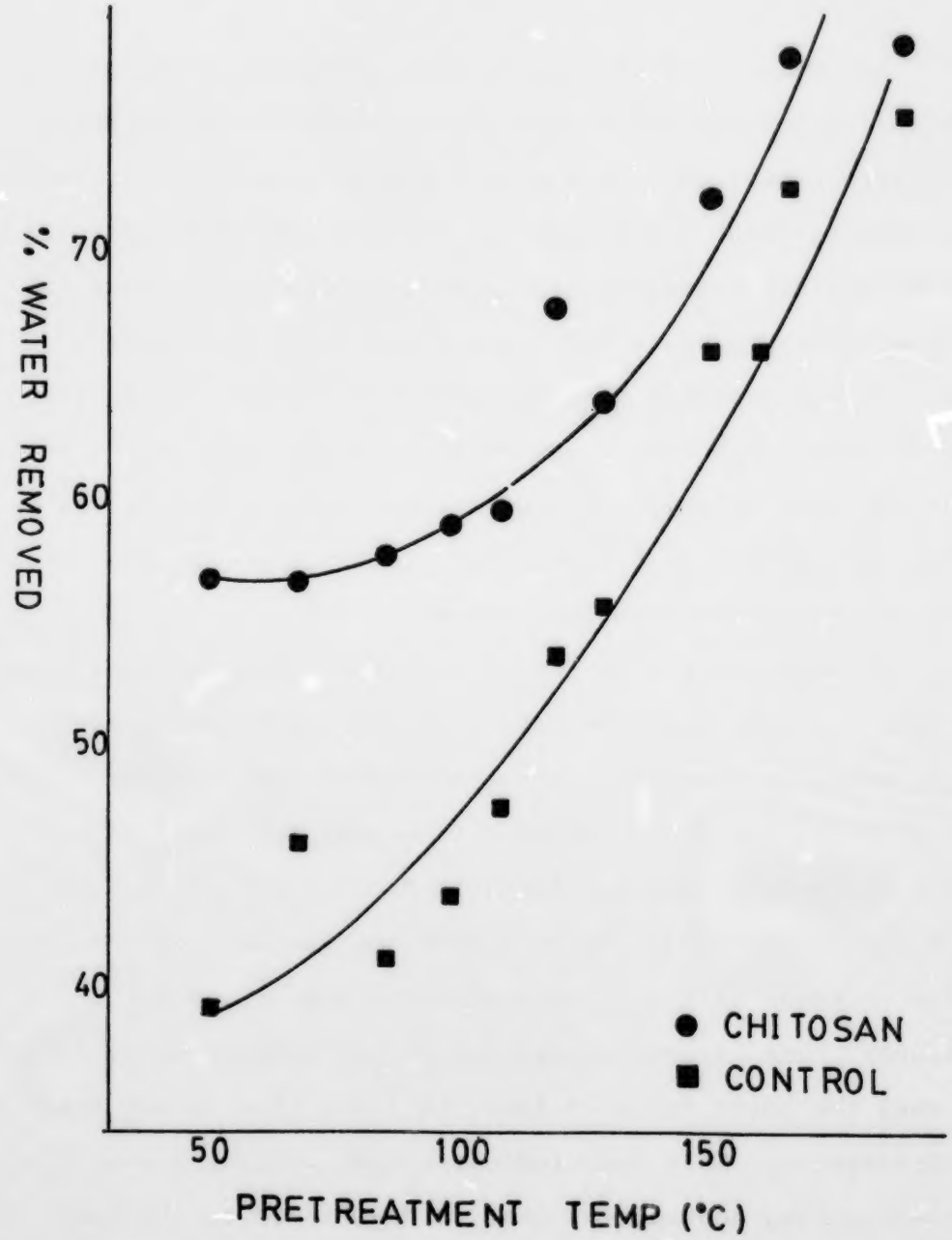
6.5 COMBINED CHEMICAL AND THERMAL PRETREATMENT

Once the preliminary heat treatment work had been completed, the focus moved to determining the effects of combining thermal and chemical pretreatment. As described in Chapter 6, cationic polymers added to peat increase the amount of water removed during pressing. Several polymers were shown to be very effective. One, the chloride salt of chitosan, which is produced in the cell walls of microorganisms, is the biological polymer we had done the most work with. Therefore, it was added to peat after heat pretreatment at several temperatures.

Three-hundred gram samples of raw peat were heated to ten temperatures between 50° and 200° C. After heating, three 25 gram samples were pressed and the average amount of water removed from each temperature is plotted as a square in Figure 6.7. The remaining heat treated peat was mixed with the optimum concentration of chitosan salt and again, 3 samples were pressed; the average amount of water removed is plotted as a circle in Figure 6.7.

Figure 6.6 shows that heat treated samples which were treated with chitosan salt consistently released more water when pressed than the control samples heated to the same temperature. However, as the temperature increases the two curves begin to converge. At 100° C there is a 10% difference between the curves and at 175° C the difference is down to about 4%. Two conclusions can be made from this data: (1) at all temperatures studied the chloride salt of chitosan and thermal pretreatment have an additive effect and (2) the enhancement is greatest at the lower tem-

FIGURE 6.7. The percent water removed after pretreatment vs. the temperature. The lower curve is data from thermally pretreated samples (■) and the upper curve is data form samples pretreated thermally and with chitosan salt (●).



peratures and lessens with an increase in temperature.

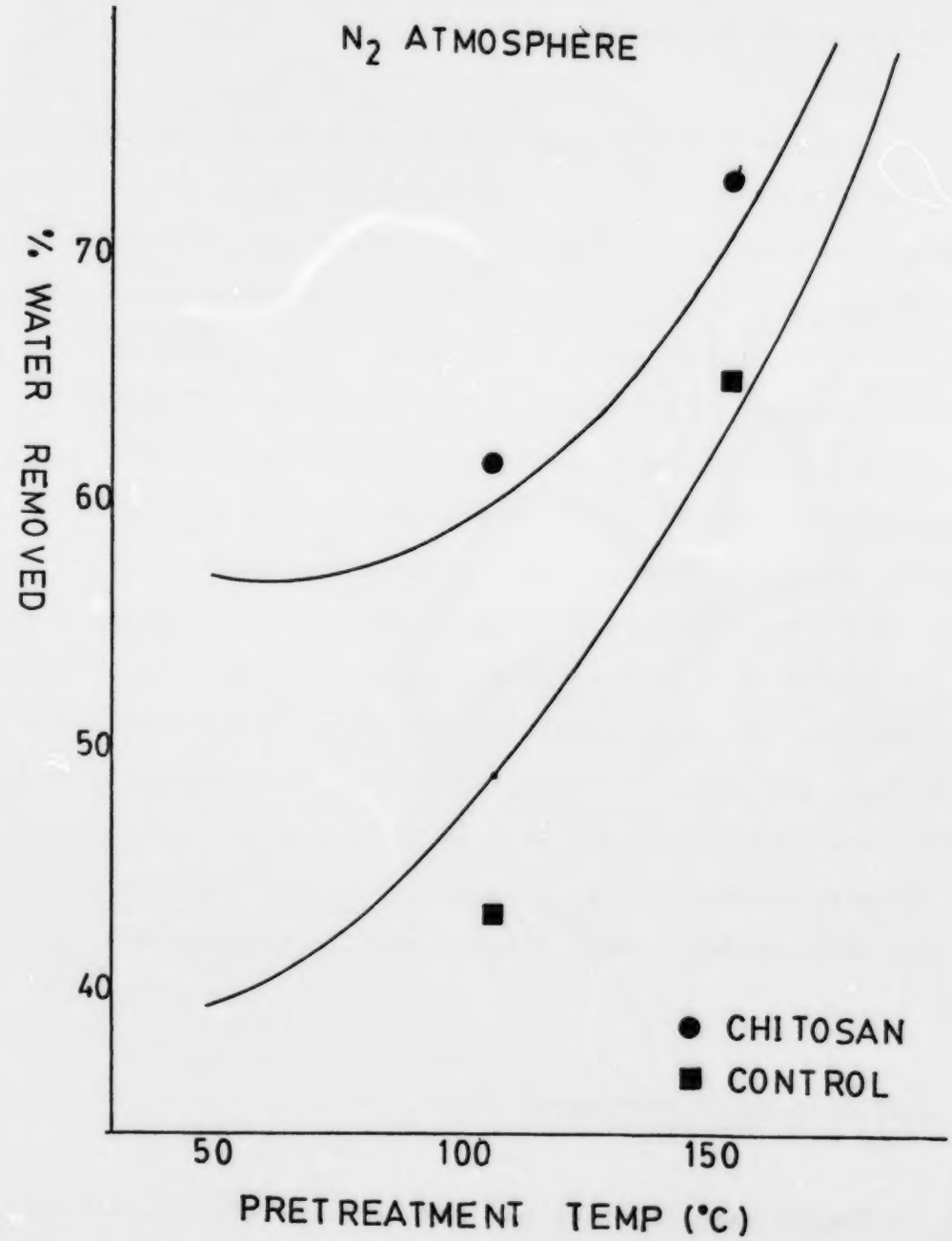
6.6. HEAT TREATMENT WITH AN INERT ATMOSPHERE

As outlined in Chapter 1, peat undergoes chemical changes during heating which facilitate mechanical de-watering. This research proves de-watering is enhanced even after low temperature pretreatment suggesting low temperature reactions. In an attempt to further characterize our low temperature process the standard heating procedure was run with an inert atmosphere.

In the standard heating procedure the two liter pressure vessel contains air which is sealed in with the peat during heating. In the inert atmosphere experiments, after the peat was placed in the reactor N_2 gas was used to displace the air. Then the peat was heated in the usual manner.

In Figure 6.8. the two curves from Figure 6.7. have been traced onto the graph and the data from the inert atmosphere heating experiments is plotted. The N_2 procedure was done for a 100° and a 150° C heating run. Figure 6.8. allows for comparison of the inert atmosphere data and the data from heating under air. Both the control data and the data from the samples treated further with chitosan salt fall very close to the curves at both temperatures. The largest aberration is the control point for the 100° C run; the point falls 3% from the line, this is not a significant difference. This data indicates that whether air or nitrogen is used during heating the peat is de-watered to the same extent. Therefore, any reactions taking place in this system

FIGURE 6.8. The percent water removed after thermal pretreatment in an N_2 atmosphere vs. temperature. Control (■) and chitosan salt treated (●) data are plotted with the curves from Figure 6.7.



which effect the de-watering properties of peat are not dependent upon the presence of oxygen.

6.7. STIRRING DURING HEATING

Heat pretreatment experiments were run at two temperatures to determine the effect of stirring during heating on the de-watering of peat. In the standard heating experiments the peat is static during heating. Stirring might lower the resistance to heat transfer or alter the colloidal properties of peat and, therefore, increase or decrease the percent of water removed.

The Parr 4501 pressure vessel is equipped with a belt driven propeller type stirrer. The propeller was rotated approximately 100 times a minute during both heat pretreatment runs. The results from the pressing experiments are plotted in Figure 6.9. Again the curves from Figure 6.7 are shown with the stirring data for comparison. The points fall very close to the curves. The control point for the 151° C run is the most deviant; it is about 3.5% from the control curve. This is not a significant difference. Therefore, stirring at 100 rpm during heating does not alter the de-watering of heat treated peat in this temperature range.

6.8. HEAT CONTENT OF PRETREATED PEAT

Twelve samples which had been pretreated, pressed and oven dried along with one control sample (no pretreatment) were

FIGURE 6.9. The percent water removed after thermal pretreatment with stirring vs. temperature. Control (■) and chitosan salt treated (●) data are plotted with the curves from Figure 6.7.

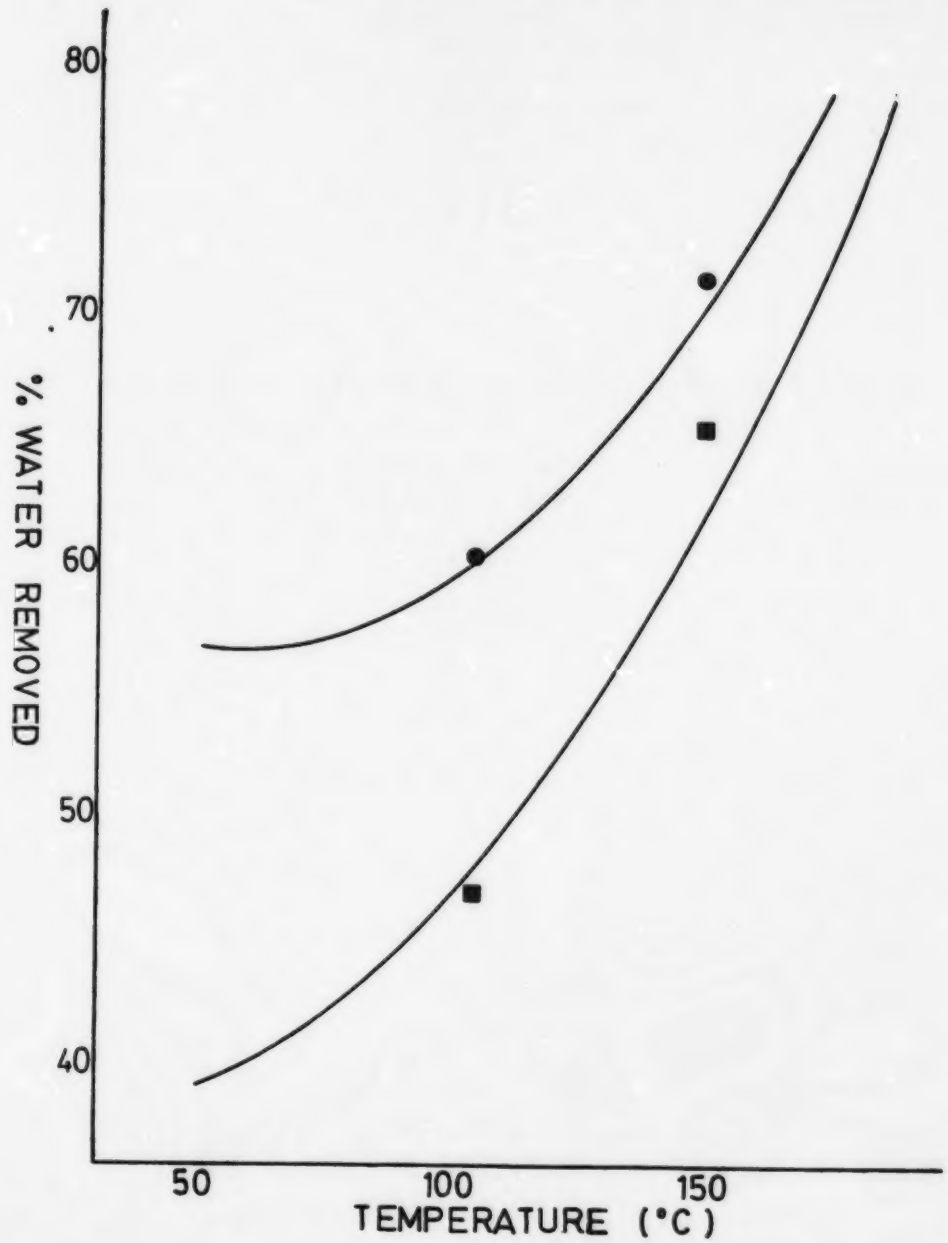


Table 6.2 A GROSS CALORIFIC VALUE ON A DRIED BASIS (kJ/kg)
PRETREATMENT WITH ZERO HOLDING TIME

PRETREATMENT TEMPERATURE (° C)	NO CHEMICAL PRETREATMENT	CHITOSAN SALT ADDED
CONTROL	22.98	
87°	22.14	22.66
100°	21.60	23.11
131°	22.55	22.82
139°	22.99	23.37
169°	23.12	22.71
192°	22.68	22.87

Table 6.2 B PRETREATMENT WITH 15 MINUTES HOLDING TIME

PRETREATMENT TEMPERATURE (°C)	NO CHEMICAL PRETREATMENT
42°	22.43
75°	22.82
100°	23.02
125°	22.68
146°	22.93
165°	22.88
197°	22.91

sent to the National Research Council laboratory in Halifax. There, the calorific value of each sample was analyzed to determine the effect of our pretreatment process on this parameter. The results are shown in Table 6.2A. The numbers show a small, random variation and no trend can be detected. The variations are probably due to the heterogeneity of the raw peat used in the pretreatment experiments. Neither, heating in this temperature range with zero holding time nor the addition of chitosan salt changes the calorific value of the dry peat.

The same analysis was also done on heat treated peat with a 15 minute holding time. The data is shown in Table 6.2B. It shows a random scatter and no significant change from the control too. Therefore, heat treatment with a 15 minute holding time also has no effect on the calorific value of the dry peat.

6.9. CONCLUSION

In the thermal pretreatment work the type of experiments which could be performed were limited by the available apparatus. Peat is sealed in the vessel, which is then placed into the heating jacket. In this procedure there is always a heat up time before the peat reaches the desired temperature. During the heat up period heat is transfered to the peat. The amount of heat transfered, a parameter which varies with the rate at which the peat is heated and the temperature to which it is heated, could not be measured or regulated with the apparatus. An alternative to the batch mode would be a continuous stirred tank reactor at

steady state in which the peat would maintain a close to constant temperature throughout its entire residence time in the reactor. However, the pumping and stirring properties of peat would create problems in this type of system.

Using the batch system, three parameters may be varied: heat up time, temperature and residence time. A change in any one of these parameters will affect the reactions described in chapter one and therefore the de-watering. Each of the three parameters was studied separately while the other two were controlled.

The first experiments, presented in section 6.2, were run while keeping the heat up time constant at 30 minutes; testing two residence times, zero and fifteen minutes; and varying the pretreatment temperature from 50°-200° C. This work leads to the following conclusions: (1) At temperatures as low as 75° C de-watering is enhanced. This confirms that low temperature reactions requiring only a small amount of heat are occurring. (2) Between 50° and 200° C both zero and fifteen minute residence times produce similar results. This indicates that the additional amount of heat added in the 15 miute runs does not promote the reactions by a detectable amount. (3) The enhancement improves rapidly up to 175° C and then levels off. This suggests that above 175° C up to 200° C the corresponding additional heat provided by our system results in almost no further reaction. Reactions which result in loss of functional groups, eg. decarboxylation and dehydroxylation, are usually characterized as low energy, low temperature reactions. As stated in Chapter 1, these are the type of reactions which are believed to result in a break

down of peat's hydrogen bonded structure and to change the water retention properties.

In the experiments described in section 6.3 the residence time was constant and two heat up times, 15 and 30 minutes, were compared at several pretreatment temperatures. In this section it was concluded that (1) more water is removed at a given temperature when the heat up time is 30 minutes and (2) the difference in the percent water removed for the two heat up times is nearly constant. A longer heat up time allows more heat to be transfered to the peat and the improved de-watering is probably due to an increase in the number or extent of the de-watering reactions. Furthermore, the fact that the difference in the amount of water removed between 15 and 30 minute heat up times is the same at all temperatures, it is possible that one type of reaction occurring is particularly sensitive to the amount of heat added (more so than to temperature) and in each of the fifteen minute heat up time runs (less heat added) this reaction is retarded to the same extent.

That reactions sensitive to the amount of heat added play an important part in determining the heat treated peat's de-watering properties is further confirmed by the data in section 6.4. In section 6.4, residence time is the variable, temperature is constant at 165° C and heat up time is 30 minutes. The data shows that an increase in residence time, therefore an increase in the amount of heat added, causes an increase in the amount of water removed. Furthermore at a residence time of 60 minutes this

effect levels off, indicating that the relevant reactions have gone to completion.

The data obtained from combined chemical and thermal pretreatment experiments also yield several conclusions. Perhaps the most important conclusion is that with the addition of chitosan salt, after thermal pretreatment, lower temperatures are necessary to remove the amount of water which would be released after higher temperature thermal pretreatment without the addition of chitosan salt. For example, in our process the pretreatment temperature required to remove 60% of the water in peat is 145° C, however, if chitosan salt is to be used a thermal pretreatment process temperature of only 105° C is necessary to remove 60% of the water. Thus, a process using chitosan salt would require less energy than a strictly thermal process.

The proposed mechanism explaining the effect of chitosan salt on peat de-watering has already been presented in Chapter 5. The same mechanism is believed to be occurring when chitosan salt is added to heat treated peat. However, this does not include an explanation for a phenomenon noted in section 6.6: as the peat is heated to higher temperatures the chitosan salt appears to become less effective. This implies that thermal pretreatment releases some of the water molecules which would have been released by chitosan salt.

Peat particles are of colloidal size and thus have a large surface area to volume ratio. They also have a net negative charge probably due to hydroxyl and carboxylic acid functional groups on molecules at the surface. A strong dipole moment caused

by the negative field of the particles exists between the oxygen and hydrogen atoms in the water layers surrounding the particles. This increases the strength of the hydrogen bonds which exist between the water layers themselves and the water layers and the peat particles. Both thermal pretreatment and chitosan salt aid in the removal of these water layers by separate but related mechanisms.

Chitosan salt, which acts as a chain of postiively charged sites, has two effects, it suppresses the negative charge on the peat particle surface and forms bridges between particles. This results in coagulation and flocculation. As the particles come together during pressing some of the water surrounding each particle is displaced and this causes a larger amount of water to be released.

Some of this same water, as well as other water molecules, is released when thermally treated peat is pressed. The reactions occurring during heating are believed to liberate several of the functional groups present in peat; carboxylic acid groups and hydroxyl groups are volatilized or rearranged during low temperature heating. The loss of these functions would have several effects. One of these would be to decrease the surface charge of the peat particles. Therefore, altering their concentration or arrangement lowers the forces binding the surrounding water layers again facilitating the displacement of these layers during mechanical de-watering.

6.10. REFERENCES

1. Chornet, E., Farrell, K., Overend, R. and Roy, C. 1981. A low severity heat de-watering technology. In the proceedings of the IGT Symposium, Arlington, Va., Dec. 1, 1981. pp. 217-237.

2. Gallo, T., Sheppard, J. 1981. Wet Oxidation of Peat. In the Proceedings of the IGT Symposium, Arlington, Va., Dec. 1, 1981. pp. 463-490.

CHAPTER 7

THE QUALITY OF EXPRESSED PEAT WATER

7.1 Introduction

In developing a peat de-watering process a parameter which must be assessed is the quality of the expressed water. The quantity of effluent released in a process designed to de-water fuel grade peat is generally 8 to 9.5 times the weight of the dried product. A medium size plant of 300,000 dry T/a would annually discharge 2.7 million cubic meters at a rate of 360 cubic meters per hour.[1] Two types of peat extract present in the effluent must be considered: the suspended solids and the dissolved organics.

In de-watering processes using strictly mechanical and/or thermal evaporation means, the liquid effluent is considered to be chemically and biochemically unchanged. In such cases only the suspended solid concentration is important. However, the typical wet carbonization process subjects peat to high temperatures and pressures. Decarboxylation occurs and peat is broken down into lower molecular weight compounds. A good amount of data has been compiled showing that many of these organic molecules are dissolved in the water released by thermal pretreatment de-watering processes.[2] The concentration of organic molecules must be monitored to insure that toxic effluent is not returned to the environment.

7.2 Toxity Tests

Microbial organisms are commonly used in toxicity tests. One such test, described is section 8.2, was used to assess the

viability of growing several different microorganisms on expressed peat water. For all the organisms tested there was no noticeable inhibition to growth after 48 hours. This indicates very low levels of toxicity. The expressed water used in these tests, however, was derived exclusively from peat which had not undergone any pretreatment process.

A second test, the Microtox test, was used to determine the effect of both chemical and thermal pretreatment on the toxicity of the expressed peat water. The Microtox tests were performed at the Ontario Research Foundation. The test employs bacteria which emit light. When they are exposed to toxic solutions, however, the amount of light emitted decreases. Basically, the percent of toxic solution which reduces the amount of light emitted by 50% is called the Ec_{50} value for that sample (actually the Ec_{50} value is estimated by graphically interpolating between values obtained from a dilution series). The higher the Ec_{50} value the less toxic the sample.

Eight samples were sent to the Ontario Research Foundation for this analysis. The results are shown in table 7.1. Measurements were taken after both five and fifteen minutes of exposure. In all cases the toxicity was very low and Ec_{50} values could only be obtained for the expressed water from samples which had been heated to 192°c in pretreatment. It would have required extrapolation beyond the data points to estimate an Ec_{50} value for the lower temperature samples.

Table 7.1: Results of Microtox Tests on Expressed Water T

Pretreatment Conditions	5 min. EC50 (% sample)	15 min. EC50 (%sample)
100°c heat treatment	VLT	VLT
100°c heat treatment and chitosan salt	VLT	VLT
131°c heat treatment	VLT	VLT
131°c heat treatment and chitosan salt	VLT	VLT
163°c heat treatment	VLT	VLT
163°c heat treatment and chitosan salt	VLT	VLT
192°c heat treatment	28%	28%
192°c heat treatment and chitosan salt	28%	28%

VLT = Very Low Toxicity

7.3 Initial Concentration of Suspended Solids

When peat is pressed mechanically the water which is released contains suspended particles. These particles may be recovered and recycled, used in the substrate in a downstream fermentation, or released into the environment. Therefore, their concentration is a parameter which must be considered in a de-watering process. Both the Zimpro's and JP Energy's de-watering processes which forms of wet carbonization. They have estimated the average concentration of suspended solids (TSS) in their effluents to be 1400 mg/l and 500 mg/l, respectively.[1]

Generally, the severity and type of pretreatment process used before pressing effects the concentration of suspended peat solids in the expressed water. Therefore, this parameter was measured for peat pretreated at eleven different temperatures with and without chitosan salt. The data is shown in table 7.2 Each entry was obained by collecting a small sample of expressed water after pressing. One milliliter of this was then diluted with 9 milliliters of distilled water, the solution was vortexed for 30 seconds and then transferred to a cuvette. The absorbance of the sample was immediately measured and the concentration was calculated using the graph described in section 4.7

In table 7.2 the lowest initial concentration of suspended peat solids is 430 mg/liter for peat which was not heated but was pretreated with chitosan salt. The highest initial concentration is 3220 mg/liter for peat which was heated to 192°c. For each pretreatment temperature studied the addition of chitosan

Table 7.2 Initial Concentration of Suspended Solid in Expressed Water.

Pretreatment Conditions	Initial Solids Concentration (mg/liter)
no heating	550
no heating & chitosan	430
to 51°c	590
to 51°c & chitosan	550
to 65°c	890
to 65°c & chitosan	760
to 87°c	460
to 87°c & chitosan	470
to 100°c	530
to 100°c & chitosan	610
to 110°c	670
to 110°c & chitosan	450
to 121°c	840
to 121°c & chitosan	600
to 131° c	1410
to 131°c & chitosan	1320
to 139°c	2750
to 139°c & chitosan	2930
to 169°c	2880
to 169°c & chitosan	2670
to 192°c	3000
to 192°c & chitosan	3220

salt does not have a significant effect on the concentration of suspended solids. However, the data clearly shows that an increase in pretreatment temperature results in an increase in suspended solids concentration.

7.4 Settling Tests

One hour after the initial concentration readings were taken a second reading was made on the expressed water samples. These two values allowed calculation of the percent of solids settled after one hour. The results are shown in table 7.3. There is no correlation between the percent settled and the pretreatment temperature. At each temperature a greater percent of suspended solids settled out after one hour from water samples pressed out of peat which was treated with chitosan salt. The average difference after one hour is 14.4%, a significant improvement for chitosan treated samples.

A third reading was also taken after 5 days had passed. For heat treated samples the concentration of suspended solids was consistently 100 ± 10 mg/l. For heat and chitosan treated samples the concentration was always less than 10 mg/l. Visually, the expressed water from samples which had not been treated with chitosan was still murky after five days and the water from samples which had been treated with chitosan salt was clear.

The rate at which the suspended peat particles settle is determined by their size. Larger particles settle faster. Thus, peat treated with chitosan salt yields expressed water with sus-

Table 7.3. Settling Tests on Expressed Water

Pretreatment Conditions	% Settled in the First Hour
no heating	5.6
no heating & chitosan	14.2
to 51°c	16.9
to 51°c & chitosan	24.5
to 65°c	13.5
to 65°c & chitosan	30.8
to 87°c	22.8
to 87°c & chitosan	30.6
to 100°c	22.5
to 100°c & chitosan	44.1
to 110°c	10.2
to 110°c & chitosan	23.1
to 121°c	15.1
to 121° & chitosan	27.0
to 131°c	15.1
to 131°c & chitosan	29.9
to 139°c	18.0
to 139°c & chitosan	28.1
to 169°c	15.8
to 169° & chitosan	29.4
to 192°c	18.0
to 192°c & chitosan	22.9

pended solid particles which are on the average larger in size than peat which is not treated with chitosan salt. This supports the theory put forth in chapter 5 explaining that chitosan salt causes coagulation. The settling tests also demonstrate two added benefits pretreatment with chitosan salt would provide in a de-watering process: (1) the faster settling rate of suspended solids will increase the efficiency of a recycle recovering peat solids and (2) the water which remains is cleaner (has a lower suspended particle concentration).

References

1. Monenco Ontario Ltd. 1983., Process Evalution and Conceptual Design of Plant Based on a Technical and Economic Assessment of Peat De-watering and Peat Fuel Processes - Phase 1 (UP-M-319-1). National Research Council Contract No. DSS. 1SX82 - 00030.

2. Washburn & Gillis Associates Ltd., Indentification of the Pollution Potentail of the harvesting and prentilization processes of peat as an Energy Commodity - Final report submitted to Environment Canada, March 1983.

Chapter 8

An Investigation of Xanthan Polysaccharide Production from Peat and/or Peat Water

8.1. Introduction

Xanthan gum is currently the most economically valuable microbial polysaccharide. Since the early 1970's thousands of tons/year have been produced for food and industrial uses. Presently it is produced by Kelco (U.S.), General Mills (U.S.), Rhone-Poulenc (France) and Tate and Lyle (U.K.). Xanthan has unique physical properties. It dissolves in hot or cold water producing high viscosity at low concentration. It is highly pseudoplastic (shear sensitive) and is temperature, salt, and pH resistant[1]. Although not a gelling agent by itself xanthan can be used in combination with locust bean gum to produce a gel[2]. It has applications in textile printing, drilling muds, rust removal agents, liquid animal feeds and especially in tertiary oil recovery (polymer flooding)[3]. Other uses are in gelled explosives (i.e. waterproof dynamite), as a paint stabilizer and as a flocculating agent for water clarification[4]. Derivatives of xanthan can also be of value. Hydroxyalkyl ethers can be used in cosmetic formulations and dialkylaminoalkoxyethers as sizes 4. Graft copolymers with acrylamide, and/or acrylic acid, and other monomers can be prepared.

The processing of peat can produce an aqueous toxic waste stream. The organic content and toxicity of the waste varies greatly with the type of process. In one particular wet carbonization process the effluent contained 8050 ppm of soluble organics of which 80% was methanol, acetic acid and acetone while the phenol content was 218 mg/L[5]. Although toxic, methanol, ace-

tic acid and acetone all can serve as good carbon sources for microorganisms. Methanol is being seriously considered as the carbon source for large-scale single-cell protein factories. It has been proposed that Acinetobacter calcoaceticus single-cell protein be produced from Sasol (coal gasification) effluent[6]. Sasol contains 1% C_2-C_5 monocarboxylic acids 70% of which is acetic acid. Even phenol can be degraded by microorganisms[7,8]). The problems caused by toxicity and the presence of multiple carbon sources can be solved by using the appropriate fermentation technique. For example Acinetobacter calcoaceticus can be grown on high concentrations of acetate and ethanol without diauxic growth or toxic effects when a carbon-limited chemostat system is employed[9]. Similarily Psuedomonas oxalaticus OX1 has been grown on a mixture of acetic and formic acids[10].

It is already well known that microorganisms can grow on peat processing wastes. Extensive pilot-plant tests have been made by Sorigoma AB in Sweden. The waste from a wet-carbonization process is treated aerobically. The resulting sludge is converted to methane and CO_2 anaerobically. BOD reduction is greater than 95% while COD reduction exceeds 75%[11]. Peat hydrolyzate (autoclaved acidic peat extract) has been used as a carbon source in batch production of pullulan by Aureobasidium pullulans[12,13]. Organic acids such as glutamic and citric acids have been shown to serve as carbon sources for Xanthomonas campestris[14]. They stimulate xanthan production by this organism. X. campestris is known to utilize acetic acid and other organic acids as its sole source of carbon[15]. It would then seem to be a strong possibility that

X. campestris could utilize components of peat waste waters to produce xanthan gum.

A study on the growth of Xanthomonas campestris in peat run-off water (Barrington peat) was begun. The use of X. campestris in a wastewater treatment scheme serves two purposes. One is the reduction of the pollution level (i.e. lowering the chemical oxygen demand (COD)) and the second is the production of a valuable microbial extracellular polysaccharide (xanthan gum).

8.2. The Effect of Medium Composition Xanthan Production

The effect of media on culture growth and production of xanthan gum was investigated. Neither culture growth nor production of xanthan gum occurred when no nutrients were added to the peat run-off water. Both a phosphorus (0.5% KH_2PO_4) and a nitrogen (0.2% $(NH_4)_2\ SO_4$) source were necessary for growth of X. campestris (Table 8.1.). It was also found that the addition of peptone or yeast extract had a positive effect on growth and xanthan gum production. When these two nutrients were added together, the growth and production were slightly higher than when they were added separately (Table 8.1.). Although, citric acid has been reported to improve xanthan production, its addition had no effect. Two other nutrients, glutamic acid and methionine, have previously proved useful in xanthan production. The addition of these components, separately and collectively, increased the xanthan production dramatically (Table 8.1.). However, biomass concentration was not enhanced to the same extent.

Table 8.1. Effects of Media on Growth of Xanthomonas campestris and Production of Xanthan Gum

Medium	Biomass (g/L)	Xanthan Gum (g/L)
1) No Nutrients Added	0	0
2) N;P	0.06	0.4
3) N;P;YE	0.31	0.6
4) N;P;PEP	0.25	0.6
5) N;P;PEP;YE	0.26	0.7
6) N;P;PEP;YE;CA	0.28	0.6
7) N;P;PEP;YE;GA	0.38	2.6
8) N;P;PEP;YE;ME	0.44	3.0
9) N;P;PEP;YE;GA;ME	0.40	2.6

N = 0.2% $(NH_4)_z\ SO_4$

P = 0.5% $KH_2\ PO_4$

CA = 0.2% citric acid

PEP = 0.01% peptone

YE = 0.01% yeast extract

GA = 0.1% glutamic acid

ME = 0.1% methionine

8.3. The Toxicity of Peat Water Towards Microorganisms

A study of the inhibitory effects of peat run-off and pressed peat water (both from Barrington peat) was initiated. A variation of the Kirby-Bauer method for determining bacterial sensitivity to antibiotics was employed to determine the inhibitory effects of the peat waters on various microorganisms. The revised method involved growing pure colonies of the various organisms in shake flasks and then innoculating standard agar plates with the organism to be tested. Then, sterile filters which had been pre-soaked in the pressed peat water or the peat run-off water were placed on the plates in various locations. Inhibition was measured using the following procedure. First, the area of clearing was calculated after 24 hours. This gave a rough initial indication of how sensitive the organism was to the peat water. Thus, the larger the area of clearing, the more inhibited the organism was to the peat water. Finally, the area of clearing was recalculated after 48-72 hours. This measurement determined if an organism could adapt to the new environment and begin to grow again normally.

The study (Table 8.2.) indicated that peat water had no dramatic effect on the growth of the organism. The greatest inhibitory effects were found with the Gram positive bacteria Bacillus subtilis and Micrococcus luteus and to a lesser extent Staphylococcus epidermidis. The gram negative bacteria Pseudomonas acidovorans, Escherichia coli and Proteus rettgeri tended to be initially inhibited but quickly adapted. The yeast Saccharomyces

Table 8.2. Inhibitory Effects of Peat Run-off Water and Pressed Peat Water on Organism Growth

Organism	Peat Run-off Water		Pressed Peat
	Area of Clearing (mm^2)		Area of Clearing (mm^2)
	Initial	Final	Initial
Bacillus subtilis	21.65	5.70	6.88
Pseudomonas acidovorans	11.78	0	14.32
Escherichia coli	8.69	0	3.37
Saccharomyces cerevisae	0	0	0
Staphylococcus epidermidis	5.70	0	5.70
Micrococcus luteus	5.00	3.37	15.62
Proteus rettgeri	0	0	16.28

Table 8.3. Growth Medium Composition

A) Mineral Salts Medium

Component	Concentration gL^{-1}
Glucose	Variable
$(NH_4)_2SO_4$	4
KH_2PO_4	2
$Na_2HPO_4 \cdot 7H_2O$	1
$MgSO_4 \cdot 7H_2O$	0.2
$CaCl_2$	0.02
Yeast Extract	0.1
$(CH_3COO)_2Zn \cdot 2H_2O$	0.016
$FeSO_4 \cdot 7H_2O$	0.003
H_3BO_3	0.006
$(NH_4)_6MO_7 \cdot 4H_2O$	0.006
HCl	0.3

pH adjusted with NaOH

B) YM Medium

Component	Concentration gL^{-1}
Glucose	10
Peptone	5
Malt Extract	3
Yeast Extract	3

cerevesiae showed no signs of growth inhibition by peat water. Most microorganisms tested showed an initial area of clearing which was subsequently totally overgrown.

Although X. campestris was not included in the above study we did other studies which showed the toxic effect of peat hydrolyzate. After finding the peat run-off water had no detrimental effect on the growth of X. campestris we attempted to grow this organism in the presence of peat hydrolyzate. Barrington peat was added to peat run-off water in a 10 g/L concentration. The pH was adjusted to 2.9 with concentrated hydrochloric acid. This was autoclaved for 15 minutes at 15 psi and 121° C. It was then filtered to remove suspended solids. This was followed by the addition of 2.0% glucose, 0.4% $(NH_4)_2 SO_4$ and mineral salts (as shown in Table 8.4.). A pH-controlled (pH=7.0) fermentation was then performed using this medium. No growth occurred. This verified that in this concentration peat hydrolyzate is toxic to X. campestris.

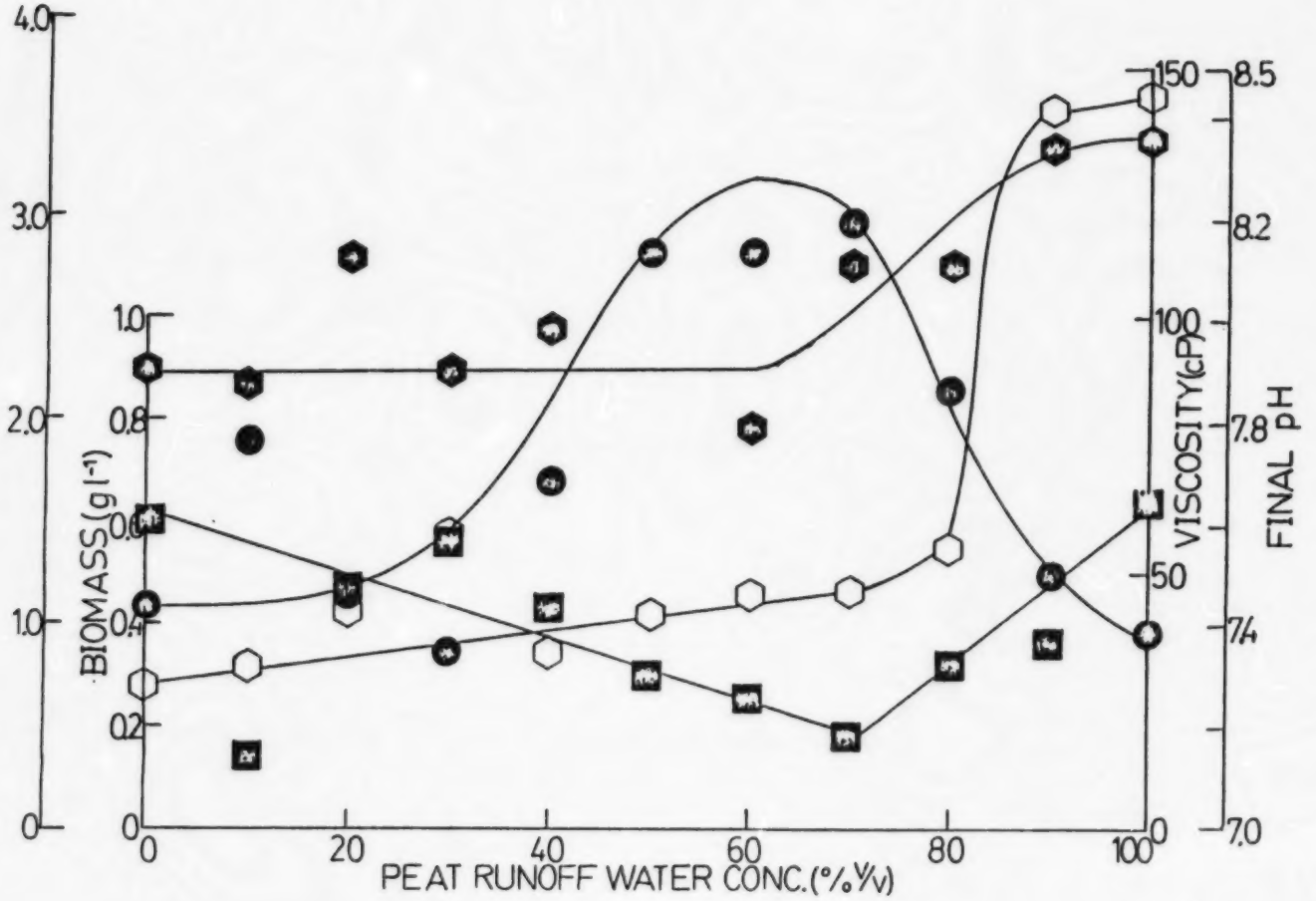
8.4. The Effect of Peat Run-off Water on Xanthan Production

Attempts were made to determine conclusively whether X. campestris could use peat run-off water as a growth substrate. One strain, X. campestris (NRC 2146), was grown on 0.8% nutrient broth made up with different concentrations of peat runoff water (Figure 8.1.). The control flasks were pH adjusted before autoclaving but after autoclaving the flasks containing peat water were more acidic. Since the pH rises to toxic levels during fer-

Table 8.4. The Effect of Peat Water on Xanthan Production in Fermentations using Mineral Salts Medium

Peat Water Present	Glucose Initial Concentration g kg^{-1}	Maximum Biomass g kg^{-1}	Maximum Xanthan g kg^{-1}	Y X/S W/W	Y P/S W/W	Y P/X W/W	Max. Visc. cP RV	Max. Visc./Max. Xanthan $cP/g^{-1}kg^{-1}$	Max. Oxy. Uptake Rate $mML^{-1}h^{-1}$
yes	5	0.98	1.6	0.20	0.318	0.162	76	48	5.4
yes	10	1.63	5.0	0.163	0.503	3.09	14	29	13.6
yes	20	2.24	11.3	0.112	0.565	5.04	75	67	11.1
yes	20	1.79	10.9	0.09	0.552	5.03	66	63	17.05
no	20	1.08	13.3	0.054	0.663	12.3	114	86	5.8
no	20	1.15	13.5	0.057	0.665	11.5	78	58	6.1

Figure 8.1. X. campestris NRC 2146 grown on 0.8% nutrient broth made up with different concentrations of peat run-off water (final biomass (■); control biomass (□); final pH (●); control pH (○)).



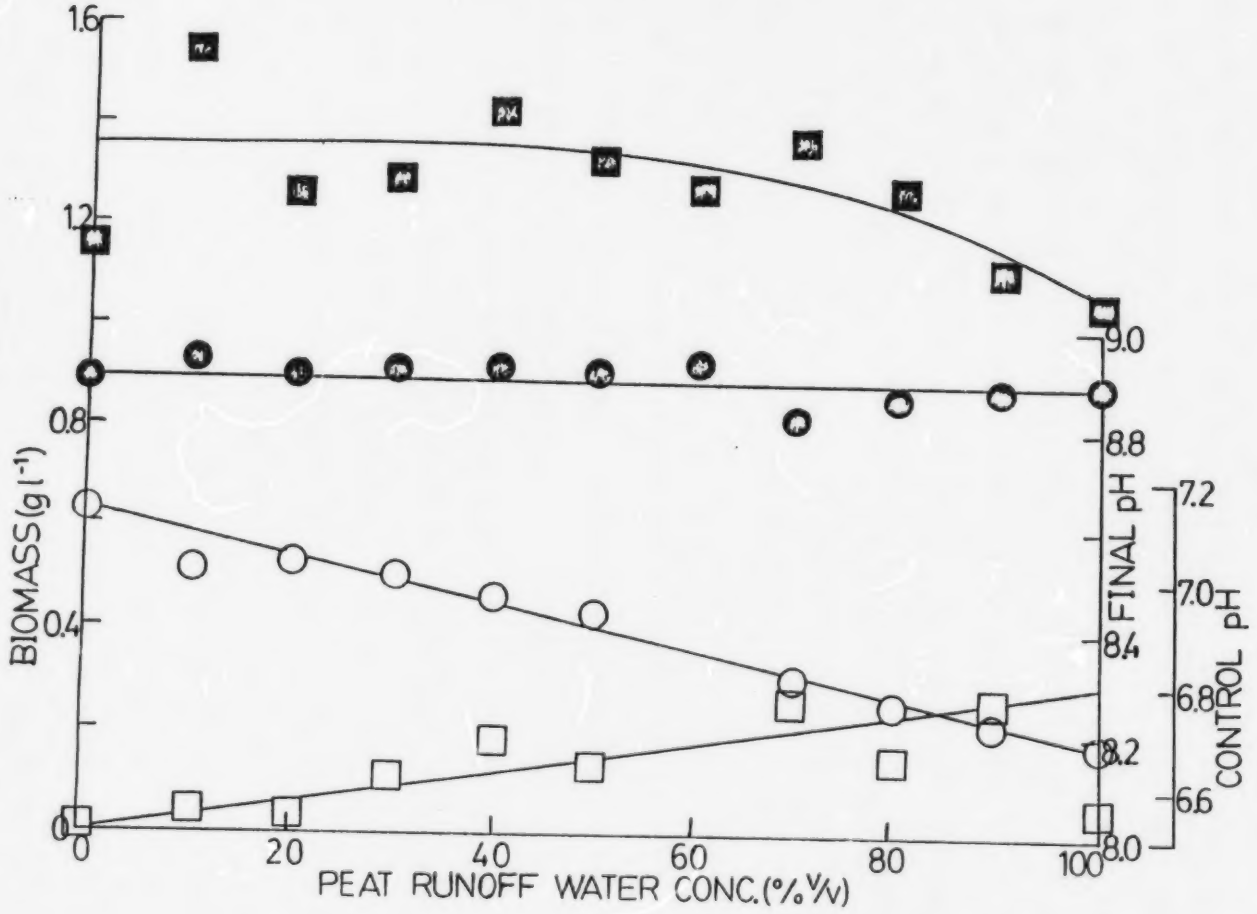
mentation, a lower initial pH could allow for more bacterial growth but this did not occur. The control flask data also showed that the peat runoff water contained 0.35 g/L (dry weight) of solids. This experiment used unfiltered peat runoff water.

After growth for 3 days at 24° C the pH in all flasks was approximately 8.9. This is very probably a toxic level and caused growth to cease. The final dry biomass in most flasks was about 1.4 g/L uncorrected for peat solids. There was slightly less biomass produced at higher concentrations of peat water. No polysaccharide was produced and the final viscosities were identical to that of water. The inoculum was 5% by volume and had been grown on nutrient broth made up solely with distilled water.

Another strain of Xanthamonas campestris (ATCC 13951) was grown on YM medium made up with various concentrations of distilled water and filtered peat runoff water (Figure 8.2.). X. campestris ATCC 13951 is the production strain developed by the Northern Regional Research Laboratory (NRRL B-1459). The composition of YM broth is given in Table 8.3. It is the medium of choice for high yield xanthan production.

In this experiment a dramatic increase in final xanthan concentration and medium viscosity was noted when the peat runoff water concentration was higher than 60% (Figure 8.2). Final biomass concentration was also slightly higher after decreasing up until that concentration. The final pH reached a maximum at 60% peat runoff water. The data indicate that either xanthan yield is higher or the rate of xanthan production is faster when peat runoff water is used. The culture had been grown for 2.5 days at 24°

Figure 8.2. X. campestris ATCC 13951 grown on YM medium with different concentrations of peat run-off water (biomass (■); pH (final) (●); xanthan production (⬢); viscosity (○)).



C. The inoculum had been grown on YM broth made up with distilled water.

In order to verify that the presence of peat run-off water in the production medium resulted in increased production of xanthan gum by X. campestri (ATCC 13951) and to determine the causes of this effect we chose to run pH-controlled batch fermentations using either peat run-off water or distilled water to make up the medium. Previously, when using shake-flasks, we had generally used a rich organic medium such as YM medium but for the fermentation study we chose to use a mineral salts medium with glucose as the only carbon and energy source. The results of this study are shown in Table 8.4. They show that when peat run-off water is used in place of distilled water more biomass but less xanthan is produced. Also the gum that is produced in the presence of peat run-off water is slightly less viscous. The maximum oxygen uptake rate is higher when peat run-off water is present. This is probably due to the higher maximum biomass concentration but may also indicate co-oxidation of extracted peat materials. In all cases, the glucose had been totally utilized well before monitoring of the fermentation had ceased so the yields are based on total glucose consumption.

We also ran fermentations in which we varied the initial glucose concentration of media made up with peat run-off water. The results of these fermentations are shown in Table 8.4. and Figure 8.3. In Figure 8.3., we have interpolated the data towards the zero point on the x-axis. This was done in order to find the effects of using no glucose. If we had performed an actual fer-

mentation with peat run-off water but no glucose, the data values would have been too small to be of reliable accuracy so we used this method instead. Figure 8.3. indicates that if no glucose was supplied, then no biomass would have been produced. It also indicates that the final medium viscosity would be similar to that of the initial inoculated medium and that approximately 0.25% w/v glucose would be required to produce any xanthan.

This discouraging data stimulated us to repeat a previous shake-flask experiment in which we varied the amount of peat run-off water used instead of distilled water to make up the YM medium. The results, after 3 days growth, are shown in Figures 8.4.A and 8.4.B. They indicate that up to a concentration of 70%, peat run-off water stimulates biomass concentration. They also indicate that the final xanthan concentration is directly dependant on the amount of peat water in the medium and that final viscosity is greatly increased by the presence of peat run-off water. Figure 8.4.B also shows that pH is not a significant factor.

The vast difference in results between shake-flask experiments using YM medium and fermentor experiments using a defined medium caused us to look more closely at the two media employed. Their compositions are given in Table 8.3. We hypothesized that peat run-off water may contain a trace element that is missing in YM medium but present in the defined mineral salts medium. We, therefore, repeated the shake-flask experiment but used a mineral salts medium with 2% w/v glucose rather than YM medium. The results are shown in Figure 8.5. Figure 8.5. indicates that peat run-off water has little effect on biomass or xanthan produc-

Figure 8.3. The effect of adding glucose to a mineral salts medium made up with peat run-off water
(maximum biomass concentration (○); maximum viscosity (□); maximum xanthan concentration (△)).

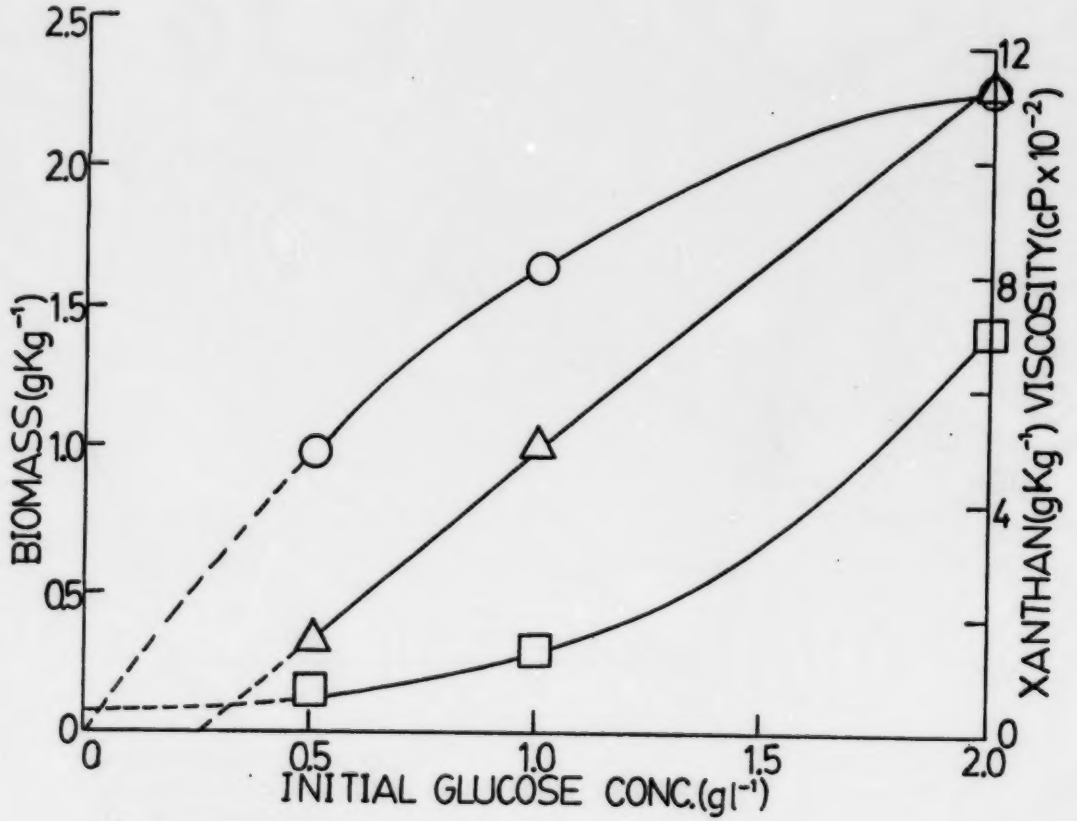


Figure 8.4.A The effect of the presence of peat water on xanthan production in YM medium in shake-flasks
(biomass concentration (Ô); xanthan concentration (Δ)).

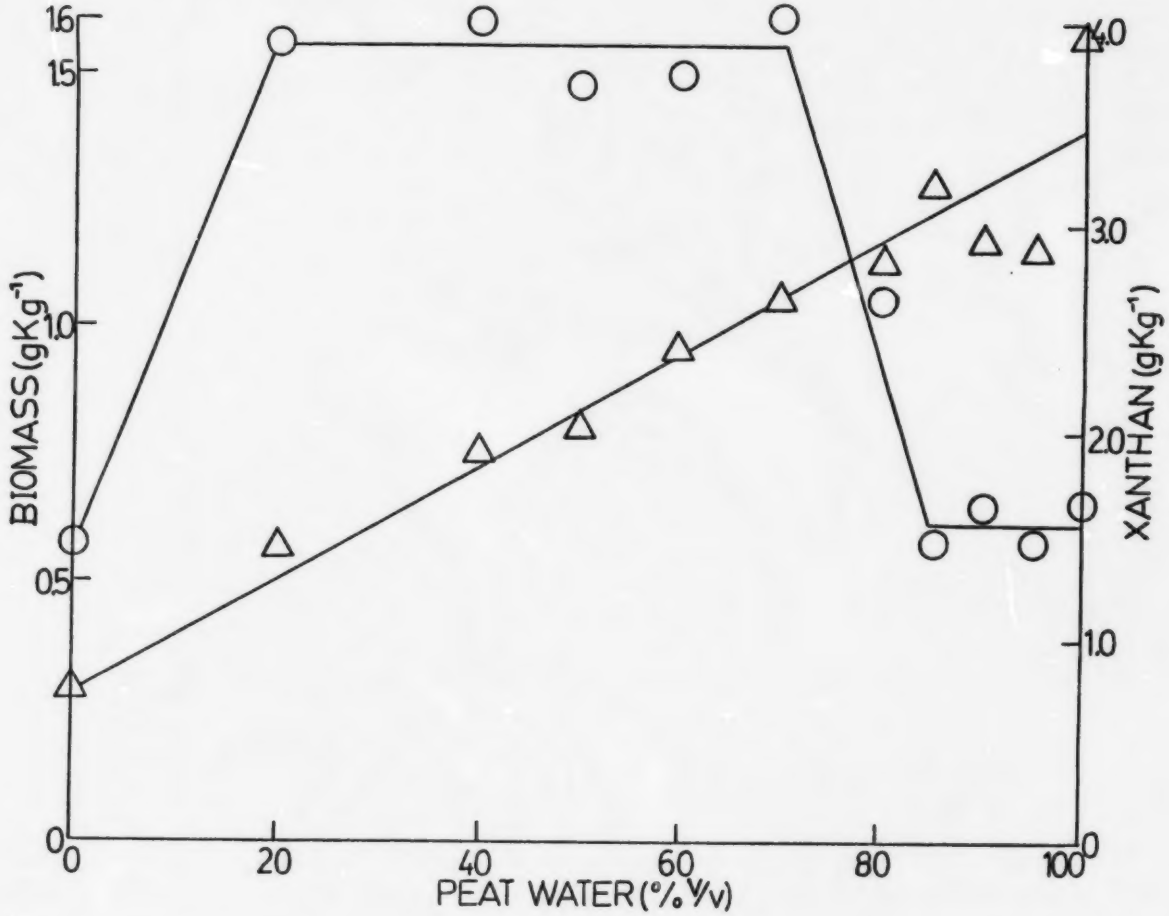
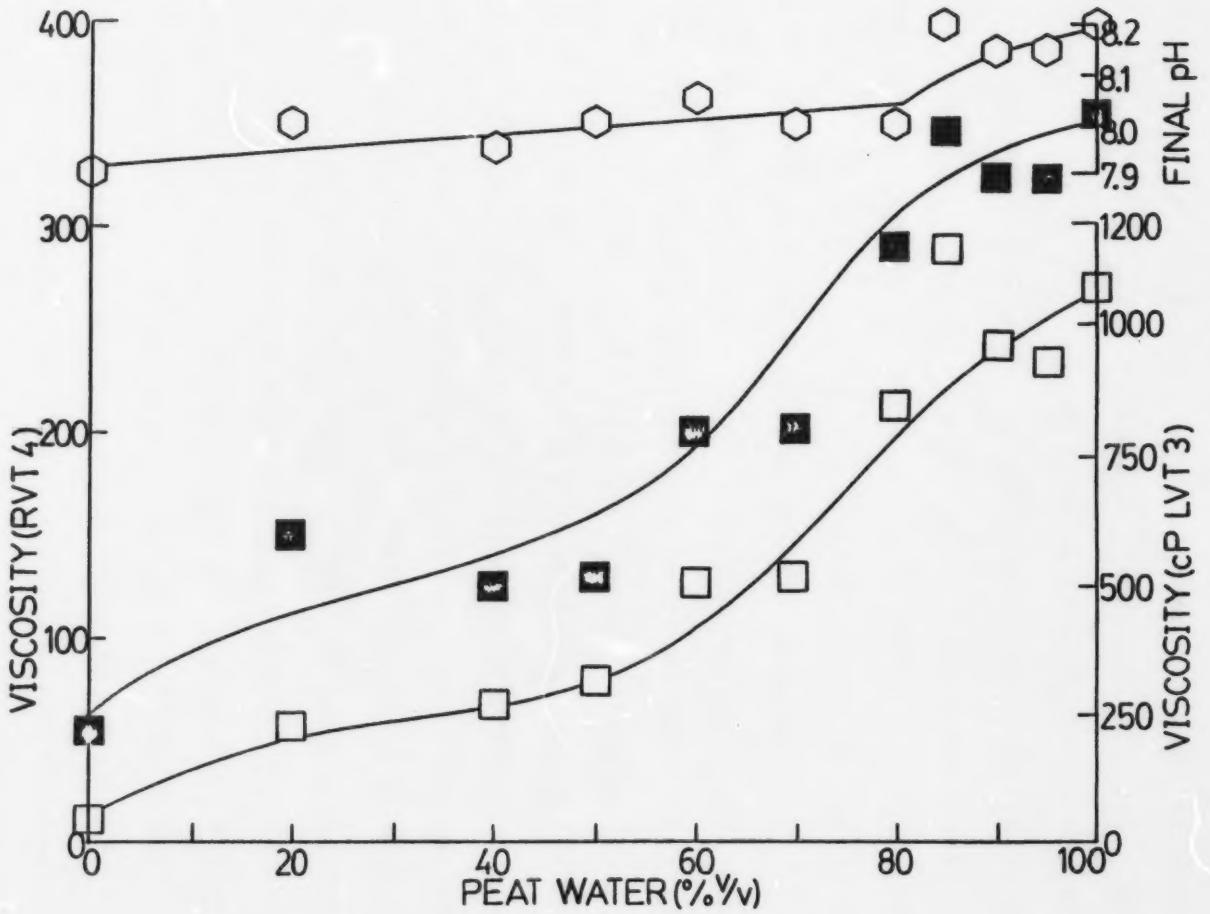


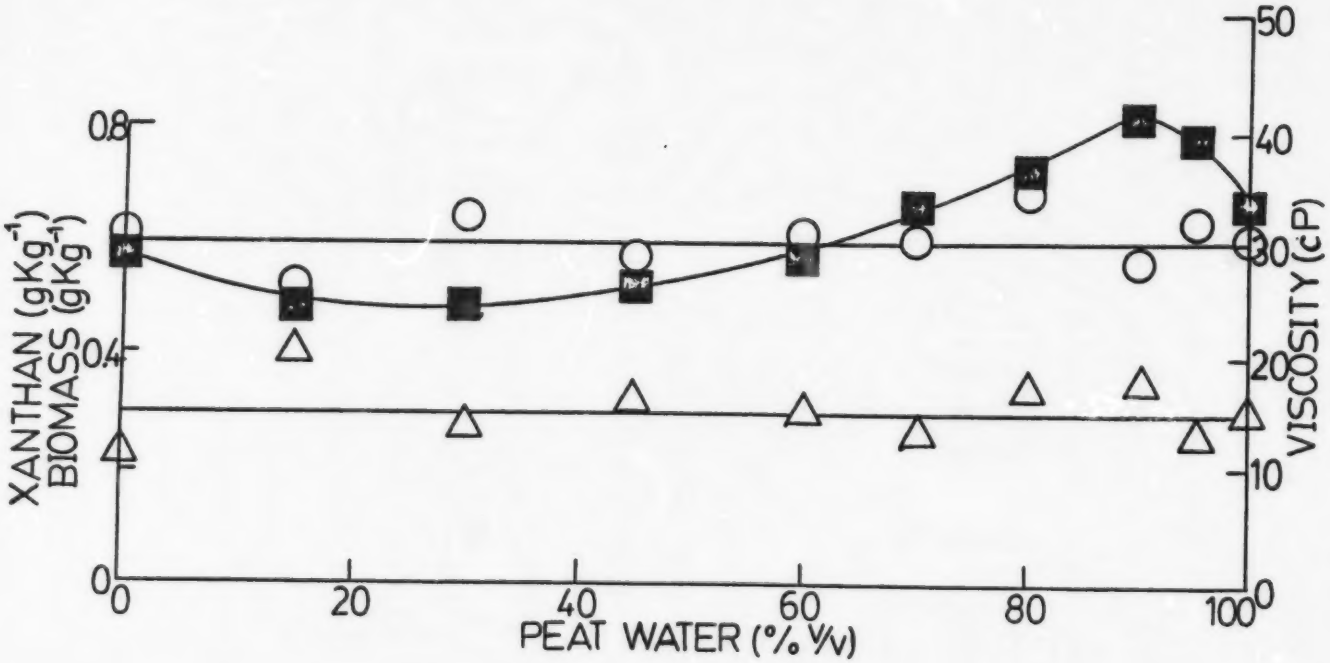
Figure 8.4.B The effect of the presence of peat run-off water on xanthan production in YM medium in shake-flasks
(pH (⬡); viscosity (Brookfield RVT4, 100 rpm, 1 min) (□); viscosity (Brookfield LVT3, 30 rpm, 1 min) (■)).



tion in this medium although final viscosity was slightly improved. The results shown were taken after 3 days growth at 28°C. Glucose analysis showed that less than 25% of the glucose had been used although all other medium components were in excess. We then repeated this experiment hoping for greater production if we sampled at a later time but after 11 days the results were similar to those shown in Figure 8.5.

We were able to draw several conclusions from these results. One was that good oxygen transfer is necessary for good xanthan yield especially when using a mineral salts medium in place of a rich organic medium. This fact is already well known in the biopolymer industry. It seems that peat run-off water does supply something that stimulates the rate of xanthan production in YM medium. This factor is probably a trace element that is present in the mineral salts medium and is of little economic value. Further research would be needed to verify this. However, the batch fermentation data strongly indicate that there is no carbon source in filtered peat run-off water that is both present in any sizeable quantity and is utilizable by X. campestris. Peat hydrolyzate was shown to be toxic. Never-the-less the toxic materials present in peat hydrolyzate may be utilizable by X. campestris under conditions of carbon limited chemostat or fed-batch culture. Under these conditions the toxic components are metabolites and thus never allowed to reach a toxic concentration. Xanthan has been produced successfully on a laboratory scale under chemostat conditions[16]. This is not recommended however since the yield of xanthan decreases steadily as the dilution rate of the culture is

Figure 8.5. The effect of the presence of peat run-off water on xanthan production in a glucose mineral salts medium in shake-flasks (3 days) (biomass concentration (○); viscosity (■); xanthan concentration (△)).



increased making the process uneconomical. Fed-batch production is practised, however, since this method of production overcomes the problem of oxygen limitation prevalent in regular batch fermentations of X. campestris. Therefore since it is known that toxic components of peat hydrolyzate such as acetic acid are utilizable by X. campestris fed-batch production of xanthan from peat hydrolyzate (as opposed to peat run-off water) may be possible.

8.5. REFERENCES

1. Cottrell, I.W. 1979. Industrial Potential of Fungal and Bacterial Polysaccharides. Presented at ACS Symposium, Hawaii.
2. Pedersen, J.K. Food Chem. 6:77(1980).
3. Wells, Jeremy. 1977. Extracellular Microbial Polysaccharides-A Critical Overview. In: P.A. Sandford and A. Laskin (eds.) Extracellular Microbial Polysaccharides, A.C.S. Symposium Series No. 45, A.C.S., Washington, pp 293-313.
4. Kang, K.S. and Cottrell, I.W. 1979. Polysaccharides. In: Peppler, H.J. and Perlman, D. (eds.) Microbial Technology, 2nd ed., vol. I, pp 418-481.
5. Washburn and Gillis Associates Ltd., Identification of the Pollution potential of the harvesting and preutilization of processing of peat as an energy commodity. Final Report submitted to Environment Canada, March, 1983.

6. Du Preez, J.C. and P.M. Lategan. South African Food Rev. 9:76 (1980).

7. Evans, W.C. Biochem. J. 41:373 (1947).

8. Pawlowsky, V., Howell, J.A. and Chi, C.T. Biotechnol. Bioeng. 15:905(1973).

9. Du Preez, J.C., Toerien, D.F. and Lategan, P.M. European J. Appl. Microbiol. Biotechnol. 13:45(1981).

10. Dijkhuizen, L. and W. Harder. Arch. Microbiol. 123:47(1979).

11. Frankel, I. and Drabkin, M. 1984. Wastewater Treatment Systems for Synthetic Fuels Plants based on Peat and Oil Shale. Presented at the A.I.Ch.E. National Meeting, Aug. 19-22.

12. Boa, J.M. and A. LeDuy. Appl. Environ. Microbiol. 48:26(1984).

13. LeDuy, A. and J.M. Boa. Can. J. Microbiol. 29:143(1982).

14. Souw, P. and Demain, A.L. J. Ferment. Technol. 58:411(1980).

15. Buchanan, R.E. and Gibbons, N.E. 1974. "Bergey's Manual of Determinative Bacteriology". The Williams and Wilkins Co., Baltimore, Md., U.S.A.

16. Silman, R.W. and P. Rogovin. Biotechnol. Bioeng. 14:23(1972).

Chapter 9

Use of a Xanthan Gum Derivative as a Water Removal Agent

9.1. Conversion of Xanthan Gum into a Charged Polymer

Xanthan Gum, which is produced by Xanthomonas campestris, is a valuable biological product. As a negatively charged polymer it is not effective as a peat de-watering agent. However, the carboxylate groups in the polymer can be modified to introduce positive charges.

Initially, ethanolamine was treated with HCl to form an ammonium salt (Figure 9.1.). Next, the carboxylate group was converted from the salt to the acid form also employing HCl. The xanthan was then heated with the hydroxylethyl ammonium chloride to afford the desired derivative (Figure 9.1.). The chemical analysis (Table 9.1.) varified the formation of the derivative and it was tested for its ability to enhance mechanical water removal from peat.

9.2. Enhanced Water Removal from Peat Using a Derivative of Xanthan Gum

The results (Table 9.2.) indicated that this derivative does improve water removal. When 0.06g of the derivative was added to peat samples 58.7% of the water present was removed. This is far superior to the control (no derivative) which removed only 28.0% under mechanical pressing. However, the results using the xanthan gum derivative are inferior to the polyelectrolytes, in particular chitosan and some of the inorganic salts tested (see Chapter 5).

Figure 9.1. Transformation of Xanthan Gum

$$HOCH_2CH_2NH_2 + HCl \rightarrow HOCH_2CH_2N^+H_3\ Cl^-$$

1

$$R\text{-}COO^-\ K^+ \xrightarrow{HCl} R\text{-}COOH$$

xanthan gum

$$\Delta \downarrow HOCH_2CH_2N^+H_3Cl^-$$

$$R\text{-}\overset{O}{\overset{\|}{C}}OCH_2CH_2N^+H_3Cl^-$$

derivative

Table 9.1. Elemental Analysis of the Xanthan Gum Derivative

Element	Calculated (%)	Found (%)
Carbon	42.8	39.3
Hydrogen	6.0	5.7
Nitrogen	5.1	3.4
Oxygen	39.5	48.3
Chloride	10.9	8.7

Table 9.2. The Effect of the Derivative of Xanthan Gum in Enhancing Mechanical Water Removal From Peat

Ratio of Derivative to Peat (wt/wt)	Amount of Water Removed (kg H_2O/kg dry peat)	Water Removed (%)	Moisture Content of Pressed Peat (%)
control	1.94	28.0	83.3
0.015	3.60	52.0	76.9
0.022	4.06	58.7	74.1

Total Water Content = 6.92 kg H_2O/kg dry peat

% Water Content = 87.4%

It is apparent from this investigation that the xanthan gum derivative does improve water removal from peat. It has already been demonstrated that xanthan gum can be produced by growing X. campestris on the expressed peat water. Although this compound is not as effective as some of the other polymers tested, if the yield from fermentations on peat extracts can be improved this could be an economically acceptable additive.

CHAPTER 10

CONCLUSIONS

10. CONCLUSIONS

Microbiology can be applied to several aspects of peat de-watering to improve the economics of this process. These applications can be included with other treatment procedures. In particular, the combination of microbial and thermal pretreatment steps is extremely efficacious.

The addition of the chloride salt of the biopolymer chitosan significantly improves the mechanical de-watering of water from peat. The mechanism is an aggregation of the colloidal particles, displacing some of the water surrounding each particle. This polymer is a positively-charged polyelectrolyte. The positive charges suppress the negative charge on the colloidal particles, allowing coagulation and water release. The polymer can also flocculate the particles by bridging between them.

Other positively charged additives also improve de-watering. Synthetic polyelectrolytes are as effective as chitosan but would prove more expensive for large scale applications. Salts such as $FeCl_2$ or $AlCl_3$ aid water loss but are not as effective as the polymers. The addition of these salts would not be acceptable as this would increase the mineral content of the finished product.

The addition of chitosan can be applied in conjunction with thermal pretreatment. Heating the peat, even to relatively low temperatures, before pressing causes a significant improvement in water loss. The heating allows reactions such as decarboxylation to occur. The loss of polar functional groups from the peat

solids decreases the amount of water retained by hydrogen bonding. The addition of chitosan to heat pretreated peat results in an even larger water loss. The effects of the two pretreatments are additive. It would be possible to choose an optimum combination of thermal pretreatment, chitosan addition and thermal drying after pressing to obtain dried peat at the lowest possible cost.

The chitosan has a secondary effect on the economics of the process. If this agent is added before pressing the particles in the expressed water are larger than the control experiments. This means that the particles settle faster. These systems yield a clear aqueous phase and a sludge. The clarified water reduces costs of pollution abatement and the solids can be recycled to the press to improve final product yield.

The final use for microorganisms is to treat the carbonaceous materials dissolved in the expressed water. No matter what pretreatment processes are applied to the peat, there will be very large quantitites of water with high BOD values. This can be used as the basis of fermentation media to grow microorganisms which produce valuable products. In particular, this method can be used to synthesize the de-watering agents such as chitosan. The effluent water from the fermentor will have a lower BOD than the original stream from the press.

Thus it is possible to have a cyclic process where the waste water is used to produce the de-watering additives and the bulk of the water from the original peat slurry is returned to the environment.

APPENDIX A

ECONOMIC EVALUATION OF DE-WATERING PROCESSES *

* Tests using our additives and heat pretreatment conditions would have been run on the NRC's scaled-up equipment had there not been a reduction in funds. Data from these tests was to be used to perform a complete economic evaluation. As this was not possible, this appendix includes an economic evaluation similar to that in part 1 of this report.

ECONOMIC EVALUATION OF DE-WATERING PROCESSES

An analysis was performed to determine the economic feasibility of using biochemical pretreatment for de-watering peat. The capacity of the plant would be 270,000 dry tonnes/year of dry peat. The moisture content of the product would be 10% from a 93% water content slurry feed.

Several processes will be considered:

- Pretreatment of peat with chitosan salt (Barrington peat)
- Pretreatment with a synthetic polymer, Praestol 444K (Bayer) (Barrington peat)
- Pretreatment with surfactant produced by B. subtilis (Barrington peat)

The amount of water released by pressing based on a year of production is shown for each of these processes in Table A.1. The pressate obtained after pretreatment with biological products is then used entirely for fermentation proposes. Included also in the same table is the percentage moisture of the peat after pressing. The amount of water removed increases substantially as moisture content of the peat is decreased. To determine the material balances, it has been assumed that there is a 4% loss of peat fines during pressing and a 1% loss during thermal drying (17).

The analysis is divided into 4 parts: cost of the de-watering agent, cost of preheating, cost of pressing and cost of drying.

Table A.1. Amount of Water Released During Pressing And Moisture Content of Pressed Peat After Pretreatment[a] (270,000 dry tonne peat/yr)

De-watering Process	Weight of Water Removed (tonnes/yr)	Moisture Content of Pressed Peat (%)
Pretreatment with chitosan	3,130,000	70
Pretreatment with Praestol 444K	3,130,000	70
Pretreatment with surfactant from B. subtilis	2,948,000	75
Pretreatment with heat and chitosan (Barrington peat)	3,357,000	60
Pretreatment with heat and chitosan (Quebec peat)	3,433,000	55

a. Original moisture content of peat before de-watering is 93%.

A.1. PRODUCTION OF DE-WATERING AGENTS

The production of de-watering agents involves: growing the microorganism and altering the product obtained. B. subtilis, on the other hand, produces during fermentation a surfactant which becomes concentrated in the foam overflow. No further processing is required. The synthetic polymer, Praestol 444K, only needs to be purchased from Bayer.

The medium for each microorganism was considered as the same base cost. Only 0.01% of peptone and yeast extract are used. Costs were based on Sigma Chemical estimates but were reduced to market price by comparing other items to the Chemical Marketing Reporter (48). Bulk prices would still be lower, though. A small amount of molasses was used to increase the biomass of R. arrhizus for higher product yield of chitosan, even though it was not needed initially for growth to occur. This was not necessary for growth in the higher COD pressate from heat treated peat.

For chitosan extraction from the cell wall of the fungus and inducing a positive charge on the polymer, 2 mL of 1N HCl is used. The prices of chemicals were obtained from the Chemical Marketing Reporter (48).

Production rates and requirements are shown in Tables A.2. to A.5. for each de-watering agent along with the costs of the raw materials and final costs of the product. Production and use of polymers and chitosan has been optimized. Requirements for each polymer are 0.01g per 25g of peat. All excess is sold. The selling price of the chitosan salt was determined by comparing the selling prices of other flocculating agents. Chitosan was produced

Table A.2. Production Cost of Chitosan Salt (1983 Canadian dollars) (Barrington Peat)

Item	Units	Amount
Hydrochloric Acid (0.0073 kg/L)	$/yr	$2,153,000
Molasses (0.0005 kg/L)	$/yr	188,000
Peptone (0.0001 kg/L)	$/yr	2,348,000
Yeast Extract (0.0001 kg/L)	$/yr	1,761,000
Total Cost of Raw Materials	$/yr	6,450,000
Total Cost of Production[a]	$/yr	18,428,000
Amount of Chitosan Produced	tonnes/yr	2,350
Amount of Chitosan Required	tonnes/yr	1,620
Revenue from Excess Sold[b]	$/yr	7,300,000
Cost of Production After Revenue	$/yr	11,128,000
Cost of Product/Weight Dry Peat	$/tonne	41.21

a. Raw materials taken as 35% of total cost.

b. Product can be sold at $10/kg.

Table A.3. Cost of Synthetic Polymer Praestol 444K (1983 Cdn. dollars) (Barrington peat)

Amount Required	1620 tonnes/yr
Total Cost	$16,767,000/yr
Cost per Tonne Dry Peat	$62.10/tonne

Table A.4. Production Cost of Surfactant from B. subtilis (Barrington peat)

Item	Units	Amount
Peptone (0.0001 kg/l)	$/yr	2,211,000
Yeast Extract (0.0001 kg/l	$/yr	1,658,000
Total Cost of Raw Materials	$/yr	3,869,000
Total Cost of Production[a]	$/yr	11,054,000
Cost of Product/Weight Dry Peat	$/tonne	40.94

a. Raw materials taken as 35% of total cost.

Table A.5. Production Cost of Chitosan Derivative Used With Heat Pretreatment (1983 Cdn. dollars) (Barrington peat)

Item	Units	Amount
Hydrochloric Acid (0.0073 kg/l)	$/Yr	2,308,000
Peptone (0.0001 kg/l)	$/Yr	2,518,000
Yeast Extract (0.0001 kg/l)	$/Yr	1,888,000
Total Cost of Raw Materials[a]	$/Yr	6,714,000
Total Cost of Product	$/Yr	19,183,000
Amount of Chitosan Produced	tonnes/yr	2,518
Amount of Chitosan Required	tonnes/yr	1,620
Revenue from Excess Sold[b]	$/yr	8,980,000
Cost of Production After Revenue	$/yr	10,203,000
Cost of Product/Weight Dry Peat	$/tonne	37.79

a. Raw materials taken as 35% of total cost.

b. Product can be sold at $10/kg.

at a rate of 0.75g/L. Surfactant produced by B. subtilis was only enough for use. In order to determine the total production cost, the main raw materials were taken as 35% of the cost (49). These costs are shown for each de-watering agent.

Chitosan salt was found to be the least expensive of the de-watering agents to produce in the unheated peat water and therefore the cost was evaluated also in the heat treated peat water. Due to the increase in the amount of water removed, more chitosan can be produced, making the process less expensive.

Production of these biological de-watering agents lowers the COD of the pressate, eliminating the need for pollution treatment.

A.2. PRESSING

In all processes, the cost of de-watering with a Larox filter press was assumed the same (Table A.6.) (17). This type of press, which is different from those described earlier, works automatically in a semi-continuous batch mode and is available in vertical and horizontal configurations. A feed of 6% solids can be accommodated. Little power is used, which accounts for the low cost of operation. Its parts include filter plate frame, cloth drive closing device, cloth tensioning device, and cloth centering device. The unit can be controlled by either a short or extended program.

A.3. DRYING

Flash drying, which has been used reliably for fuel peat drying is evaluated. These driers are manufactured by Outokumpu. Using the data obtained from Monenco (17), alterations were made

Table A.6. Economic Analysis of Larox Filter Press (1983 Cdn. dollars) (17)

Item	Units	Amount
Capital Investment	$	15,426,000
Annual Capital Charges (CRF=0.159761)	$/Yr	2,465,000
Annual O & M Costs	$/Yr	935,000
Annual Variable Costs	$/Yr	1,350,000
Total Annual Costs	$/Yr	4,750,000
Cost of Pressing/Weight Dry Peat	$/tonne	17.59

Table A.7. Breakdown of Operating and Maintenance Costs for Flash Drying Peat from 75% to 10% M.C.

No.	Item	Basis of Cost	Total Annual Cost
1.	Operating Labour	49 x $35,000/Yr	1,435,000
2.	Administration & Overload	60% of 1	861,000
3.	Supplies	30% of 1	431,000
4.	Maintenance	3% of Total Plant Cost (77.8% of Total Capital Investment)	1,800,000
	Total	$/Yr	$4,527,000

according to the amount of water removed. Moisture contents of 75%, 70%, 60% and 55% must be lowered to 10%.

Assuming that the energy to remove the water (3500 kJ/kg water removed) is constant, costs were extrapolated from data when moisture content is lowered from 50% to 10%.

Capital investment costs were raised exponentially by a factor of 0.65. Annual variable costs were directly proportional to the amount of heat required. Operating and maintenance costs were obtained from the operating labour and capital costs as shown in Table A.7.

Each set of costs is represented in Tables A.7. to A.11. for each of the moisture levels mentioned earlier (Table 11.1.). Drying costs substantially decrease with moisture level.

A.4. ECONOMIC COMPARISON OF THE VARIOUS DE-WATERING PROCESSES

All economic data of the various de-watering processes are presented in Table A.12. Three columns not discussed earlier are included. The first is the cost of storage. This includes the cost of storing the peat slurry for 30 days and then pumping it to the de-watering plant (17). Another item is effluent treatment. A two-stage anaerobic/aerobic digestion is required for the JP-Energy Process (17) and the methane produced in the first stage is used as fuel for the drying stage. In our processes, the water is aerobically treated by microbial production of agents that can either be sold or used as de-watering aids. The last item is heat pretreatment. For our processes, treatment is for 10 minutes as compared to the J.P.-Energy which uses a treatment of 210°C for 30 minutes.

The most expensive process is the use of the synthetic polymer

Table A.8. Cost of Thermally Flash Drying Fuel Peat From 75% to 10% M.C.

Item	Units	Amount
Captial Investment	$	$77,240,000
Annual Capital Charges (CRF=0.159761)	$/Yr	12,340,000
Annual O & M Costs	$/Yr	4,527,000
Annual Variable Costs	$/Yr	
Total Annual Costs	$/Yr	25,811,000
Cost of Drying/Weight Dry Peat	$/tonne	95.60

Table A.9. Cost of Thermally Flash Drying Fuel Peat From 70% to 10% M.C.

Item	Units	Amount
Captial Investment	$	$63,170,000
Annual Capital Charges (CRF=0.159761)	$/Yr	10,090,000
Annual O & M Costs	$/Yr	3,532,000
Annual Variable Costs	$/Yr	6,625,000
Total Annual Costs	$/Yr	20,247,000
Cost of Drying/Weight Dry Peat	$/tonne	75.00

Table A.10. Cost of Thermally Flash Drying From 60% to 10% M.C.

Item	Units	Amount
Captial Investment	$	$46,060,000
Annual Capital Charges (CRF=0.159761)	$/Yr	7,359,000
Annual O & M Costs	$/Yr	2,671,000
Annual Variable Costs	$/Yr	4,134,000
Total Annual Costs	$/Yr	14,164,000
Cost of Drying/Weight Dry Peat	$/tonne	52.50

Table A.11. Cost of Thermally Flash Drying Fuel Peat From 55% to 10% M.C.

Item	Units	Amount
Captial Investment	$	$39,700,000
Annual Capital Charges (CRF=0.159761)	$/Yr	6,343,000
Annual O & M Costs	$/Yr	2,124,000
Annual Variable Costs	$/Yr	3,313,000
Total Annual Costs	$/Yr	11,780,000
Cost of Drying/Weight Dry Peat	$/tonne	43.63

Table A.12. Comparison of Costs of Various De-watering Processes

De-watering Process[a]	Cost of De-watering Step ($/tonne dry peat)						
	Storage	Effluent Treatment	Cost of Agent	Preheating	Pressing	Drying	Total Cost
Pretreatment with Chitosan	1.28	-	41.21	-	17.59	75.00	135.08
Pretreatment with Praestol 444K	1.28	-	62.10	-	17.59	75.00	159.22
Pretreatment with surfactant	1.28	-	40.94	-	17.59	95.60	155.41
Pretreatment with heat and chitosan (Barrington peat)	1.28	-	37.79	23.36[b]	17.59	52.50	132.52
Pretreatment with heat and chitosan (Quebec peat)	1.28	-	37.32	23.36[b]	17.59	43.60	123.18
JP-Energy[c] (optimized) (210°C for 30 minutes)	1.28	15.49	-	49.00	16.73	15.19[d]	97.66

a. All costs are estimated for our de-watering processes with the exception of JP-Energy.

b. Costs are estimated for preheating at 125°C for 10 minutes.

c. Costs for JP-Energy process are based estimates given to Monenco Ontario Ltd. (17).

d. Methane produced during effluent treatment is used as dryer fuel for steam generation. Peat is used in the other drying processes.

Praestol 444K. Addition of surfactant production by B. subtilis is slightly less expensive and the cost could be further reduced by the addition of molasses. This would increase the yield of surfactant, improve de-watering ability to equal that of the polymers and thus reduce drying costs.

Chitosan is the least expensive agent due to its high sale value which cuts costs and its ability to enhance de-watering. Cost analyses were also done with peat pretreatment. Using Barrington peat, costs are $2.56/tonne less than with no heat pre-treatment. Since Quebec peat is easier to de-water than the Barrington, costs are further reduced to $123.18/tonne of dry peat.

In comparison, the JP-Energy is lower in cost due to the fact that its entire process has been optimized. Although chitosan production has been optimized to some extent our entire process has not. The ORF-Wetox process (17) costs $199.10/dry tonne of peat for a 24,750 dry tonne/year plant. The peat also has only been dried to 30% moisture compared to our 10%. Even though our plant size is larger, our process is comparable to that of the ORF.

Overall, chitosan is the most economical de-watering agent. It lowers drying costs and its production on pressates eliminates the cost of effluent treatment. Its use is also economically competitive with other de-watering processes.